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XCVI.—ON PARABROMDIMETANITROTOLUOL AND SOME OF ITS DERIVATIVES.[1]

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The work described in this paper was undertaken in order to study the behavior of a bromine atom in the ortho position between two nitro groups, but not exposed to the loosening action of a third negative group in the para position. We hoped in this way to settle two points: the ease with which an atom of bromine thus situated could be removed, and whether it might be replaced by an atom of hydrogen under the influence of sodium malonic ester, or sodic ethylate, as has been frequently observed in this laboratory[2] in the study of more highly substituted aromatic compounds.

In selecting the compound with the desired constitution we hesitated between the bromdinitrobenzol ($Br1.NO_2 2.NO_2 6$) and the bromdinitrotoluol ($CH_3 1.Br 4.NO_2 3.NO_2 5$), and selected the latter, because it was somewhat more easily prepared than the benzol compound. This selection proved an unfortunate one, so far as the first object of our research is concerned, since the parabromdimetanitrotoluol proved itself

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the Degree of Doctor of Philosophy, by Martin H. Ittner.

[2] This JOURNAL, 11, 93, 541; 12, 7, 164, 289; 13, 164: 15, 607.

a not very reactive body. C. A. Lobry de Bruyn[1] has found that in many cases the presence of a methyl group attached to the benzol ring prevents the replacement of a nitro group by an alkoxyl radical. In other words, that the methyl in toluol and its higher homologues exercises a protective action upon nitro groups, which would otherwise be easily replaced. The inertness of our parabromdimetanitrotoluol is probably, therefore, due to a similar protective action of the methyl radical upon the atom of bromine rather than to the constitution of the molecule, although this question cannot be settled until the vicinal bromdinitrobenzol has been submitted to a similar investigation.

The parabromdimetanitrotoluol was made by the reaction of Griess from the dinitrotoluidine, melting at 166°, of Beilstein and Kuhlberg.[2] It was also made by the action of nitric acid on brommetanitrotoluol, but this reaction gave much less good results than that mentioned at first. The substance melts at 118°, and is easily converted by warm aniline into the anilidodinitrotoluol, $C_6H_3C_6H_5NH(NO_2)_2CH_3$, melting-point 169°. (The nitroso derivative of this compound, $C_6H_3(C_6H_5NNO)(NO_2)_2CH_3$, melts at 123°). Sodium malonic ester did not act upon the bromdinitrotoluol under any conditions we could find although we tried the experiment under a great variety of temperatures and for different lengths of time. With sodic ethylate, on the other hand, it gave such a striking color reaction that we have decided to describe the product and those similar to it derived from allied substances in a separate paper. We will only remark here that no dinitrotoluol could be detected in the products of this reaction, and that therefore there is no evidence that the atom of bromine is replaced by hydrogen under these conditions. In fact we have not as yet found any signs of this reaction except in substances containing three or more atoms of halogen. With ammonic hydrate the bromdinitrotoluol gives dinitrotoluidine, melting at 166°; with sodic hydrate dinitrokresol, melting at 85°.

We next turned our attention to the parabromdimetanitro-

[1] Rec. Trav. Chim. Pays. Bas., 14, 95.
[2] Ann. Chem. (Liebig), 158, 342.

benzoic acid, $C_6H_2Br(NO_2)_2COOH$, which we made by the oxidation of the corresponding toluol. It melts at 181°, and, as was to be expected, is much more reactive than the parabromdinitrotoluol, since the atom of bromine is exposed to the loosening effects of the two nitro groups in the ortho position and a carboxyl group in the para position. Thus sodic hydrate in the cold converts it after some time into the corresponding oxydinitrobenzoic acid, melting at 245°–246°. We must pause here to remark that H. Salkowski[1] gives the melting-point of this paroxydimetanitrobenzoic acid as 235°–237°, but that we have proved the melting-point 245°–246° is the correct one by preparing the acid in four different ways, two of which are those given by Salkowski. With ammonic hydrate upon standing the bromdinitrobenzoic acid gives chrysanisic acid, recognized by its melting-point 259°. With aniline gently warmed a new acid was formed, the anilidodinitrobenzoic acid, $C_6H_2(C_6H_5NH)(NO_2)_2COOH$, which melts at 239°. With sodium malonic ester, at ordinary temperatures, the bromdinitrobenzoic acid was converted into the dinitrocarboxylphenylmalonic ester,

$$C_6H_2CH(COOC_2H_5)_2(NO_2)_2COOH,$$

which melts at 176°. In none of these experiments was the formation of dinitrobenzoic acid observed.

The new acids mentioned above were further characterized by the analysis of the following salts:

$C_6H_2Br(NO_2)_2COONa.4H_2O$;
$C_6H_2Br(NO_2)_2COOAg$;
$C_6H_2C_6H_4NH(NO_2)_2COONa.3H_2O$;
$(C_6H_2C_6H_4NH(NO_2)_2COO)_2Ca.7H_2O$;
$C_6H_2CAg(COOC_2H_5)_2(NO_2)_2COONH_4$.

The esters were also prepared, $C_6H_2Br(NO_2)_2COOC_2H_5$, melting at 105°, and $C_6H_2C_6H_4NH(NO_2)_2COOC_2H_5$, melting at 154°. It is perhaps worth mentioning that both these esters were made easily by the action of hydrochloric acid on the alcoholic solution, as would be expected from the recent work of Victor Meyer. The anilidodinitrobenzoic acid gave no nitroso compound with nitrous acid, whereas the anilidodinitrotoluol

[1] Ann. Chem. (Liebig), **163**, 36.

gave such a compound without difficulty, as has been mentioned already.

Some experiments on the effect of the complexity of molecules upon the properties of the substances may be mentioned here, although they did not lead to such definite results as we had hoped. Our plan was to start from the anilidodinitrotoluol, which we converted into a tribrom compound, melting at 238°, and then by making a nitro compound from this and treating it with aniline, we hoped to obtain an anilidodibromdinitranilidodinitrotoluol,

$$C_6H_3NHC_6HBr_2(NO_2)_2NHC_6H_2(NO_2)_2CH_2,$$

and by repeating these reactions to increase the chain of benzol rings indefinitely. Unfortunately the substances ceased to be crystalline very early in this work, since we could obtain crystals neither from the nitrotribrom compound, the anilido compound made from that, nor the bromanilido compound formed from the last by the action of bromine. Whether this tendency to appear in an amorphous form is due to the increasing complexity of the molecule (three benzol rings), or to peculiarities in this class of compounds can be determined only by more extended experiments. In another attempt to study this subject the amidophenylenimidodinitrotoluol, $NH_2C_6H_4NHC_6H_2(NO_2)_2CH_2$, was prepared by the action of metaphenylenediamine on bromdinitrotoluol. The reaction is much more violent than that with aniline, in fact, if no diluent is used, most of the product is charred. The substance melts at 185°, and gave a tribrom compound melting at 222°. We could not succeed in replacing the amido group by an atom of bromine.

The action of pyridine on the bromdinitrobenzoic acid was also studied. This gave two products: a white salt of pyridine, undoubtedly having the following formula, although it was too unstable to allow a good analysis,

$$C_6H_2Br(NO_2)_2COOHC_5H_5N,$$

and a yellow substance, which decomposed so easily that we were unable to analyze it. Its nature can, however, be determined from its properties and decompositions. In the first place, as it was obtained by the action of pyridine

on the white salt, it probably contains more pyridine than this substance. Its solubility in water indicates that it is a salt, and this inference is confirmed by its conversion into a red silver salt, and by the fact that pyridine is set free from it by alkalies. When crystallized from common alcohol the yellow body is slowly converted into bromide of pyridine and paroxydimetanitrobenzoic, melting-point 245°–246°. The easy solubility of pyridine bromide in alcohol proves that the yellow body could not be a mixture of this substance and oxydinitrobenzoic acid. The best explanation of the observed facts which we have been able to find is that in this substance the radical, $C_6H_2Br(NO_2)_2$, of the benzoic acid forms a salt with pyridine just as hydrobromic acid does, Br and $—C_6H_2(NO_2)_2$, combining with the atom of nitrogen. We should therefore ascribe to this substance the formula,

$$C_5H_5NBrC_6H_2(NO_2)_2COOHC_5H_5N,$$

considering it a sort of double salt of pyridine, which, when crystallized from ordinary alcohol, would break up with the water present into oxydinitrobenzoic acid, pyridine bromide and pyridine. Auwers[1] has obtained a similar addition-product from pyridine and his tribrompseudocumenol, but it seems to be somewhat more stable than ours, as it must be boiled with water in order to convert it into pyridine, hydrobromic acid and oxydibromcumenol.

We have also prepared the chlordinitrobenzoic acid which melts at 159°; and some preliminary work on the action of hydrochloric acid in a sealed tube on bromdinitrobenzoic acid showed that the products were dinitrophenol (OH 1, NO_2 2, NO_2 6), oxydinitrobenzoic acid and perhaps the as yet undescribed vicinal bromdinitrobenzol.

All the substances mentioned in this paper are derived from the bromdinitrotoluol, (CH_3 1, Br 4, NO_2 3. NO_2 5), by simple reactions, and therefore have a constitution similar to that substance.

Experimental Part.

Preparation of Dinitrotoluidine.

The dimetanitroparatoluidine which served as the starting-

[1] Ber. d. chem. Ges., **28**, 2893, 2912.

point of all our work was prepared according to the method of Beilstein and Kuhlberg,[1] but as we have introduced some alterations in the details of the process we think it best to give it in full as carried on by us. Paracettoluid was dropped in small portions at a time into well cooled nitric acid, of specific gravity 1.5 or over (obtained by distilling nitre and sulphuric acid in the proportion of 1 molecule of each). A weaker acid gave a considerable amount of mononitracettoluid. In this way we obtained an average yield of the crude dinitracettoluid, amounting to 75 per cent. of that required by the theory. The least carelessness, either in cooling the acid or in the addition of the acettoluid, reduced the yield very considerably, but in no case did we succeed in raising it much above 75 per cent. That we had formed the dinitracettoluid of Beilstein and Kuhlberg was proved by recrystallizing a little of it from alcohol, when it showed the melting-point of 191° given by them.

For the subsequent work this purification was unnecessary, so the crude dinitracettoluid was dried and then boiled with sulphuric acid of specific gravity 1.44 in a flask with a return condenser. The saponification took place very quickly after the acid had reached its boiling-point and could be followed by the change in color from yellowish-brown to dark-brown. When it was complete, the liquid was cooled in running water, diluted somewhat, and filtered; the impurities ran through, leaving nearly pure dinitrotoluidine on the filter, which, after recrystallization from alcohol, showed the melting-point, 166°, given by Beilstein and Kuhlberg. The yield was not far from quantitative. This saponification with sulphuric acid is to be preferred to that with alcoholic potash used by Beilstein and Kuhlberg, because it gives a better yield and a purer product, since the decomposition of the dinitracettoluid by the alkali is avoided, which, as Wagner[2] has found, converts it partially into dinitrokresol, and also brings about a more complete decomposition attended by the formation of potassic cyanide. Another advantage in the use of the sulphuric acid is that it dissolves any mononitrotolui-

[1] Ann. Chem. (Liebig), **158**, 342.
[2] Ber. d. chem. Ges., **7**, 536.

dine which may be present, thus avoiding the treatment of the saponified product with hydrochloric acid for this purpose, as recommended by Beilstein and Kuhlberg.

Parabromdimetanitrotoluol, $C_6H_2Br(NO_2)_2CH_3$.

This substance was prepared as follows: A quantity of the dry dinitrotoluidine was suspended in a concentrated solution of hydrobromic acid (specific gravity 1.44) and treated from time to time with small quantities of sodic nitrite, until a large excess of this reagent had been added. During this operation the liquid was kept well cooled, and the mouth of the flask was loosely corked to prevent as far as possible the escape of nitrous fumes. Since the diazo compound formed is as insoluble in hydrobromic acid as the dinitrotoluidine itself, the reaction takes place very slowly, so that it was found advisable to let small quantities of the dinitrotoluidine stand with the solution of nitrous acid for at least two days, while large quantities needed a week or more, with occasional addition of sodic nitrite and shaking. This very slow formation of the diazo compound and its insolubility probably account for the statement of Beilstein and Kuhlberg,[1] that nitrous anhydride does not act on dinitrotoluidine at ordinary temperatures. After the mixture had stood long enough, more hydrobromic acid was added, if necessary, and then the liquid was heated, care being taken to keep the contents of the flask well stirred, and to regulate the heat so that the solid portions should not melt, as, if these precautions were neglected, a smaller yield was obtained, and the product was mixed with impurities, which it was hard to remove. The product was at first purified by crystallizing it from alcohol, but later it was found that nitric acid of specific gravity 1.36 did not act on the bromdinitrotoluol, while it did oxidize the impurities, and this observation was used to improve greatly the method of purification. The crude product accordingly was treated with enough nitric acid (specific gravity 1.36) to dissolve it when boiling, and the mixture boiled until nitrous fumes ceased to come off, which indicated that all the impurities had been oxidized. The hot acid solution was then allowed to cool, when the bromdinitrotoluol crystallized

[1] Ann. Chem. (Liebig), 158, 344.

out in white prisms, which, after washing with sodic hydrate and water, were pure, if the amount of impurity in the crude substance had not been excessive. Or the nitric acid solution was precipitated with water, and, after washing with sodic hydrate and water, the precipitate recrystallized from alcohol. The substance, in whichever way purified, showed the constant melting-point 118°. It was dried at 100° and analyzed with the following results:

I. 0.1640 gram of the substance gave, by the method of Carius, 0.1185 gram of argentic bromide.

II. 0.2100 gram of the substance gave 0.1518 gram of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2CH_3$.	Found. I.	II.
Bromine	30.66	30.76	30.76

131 grams of the dinitrotoluidine gave 150 grams of pure bromdinitrotoluol instead of the 174 grams required by the theory, that is, a yield of 86 per cent. The yield varied between this and 75 per cent. in different preparations.

Properties of Parabromdimetanitrotoluol.—It crystallizes from nitric acid in white prisms apparently belonging to the trimetric system; from alcohol at first in slender curving needles somewhat branched; later these needles spread out into curving groups of rather irregular plates united by their edges, and if the plates are very well developed, rectangular forms are observed in them. It melts at 118°. It is very soluble in acetone, or ethyl acetate; freely soluble in benzol, chloroform, or carbonic disulphide; moderately soluble in ethyl, or methyl alcohol, or glacial acetic acid, and its solubility in these three solvents is increased by heat; nearly insoluble in water, or cold ligroïn, moderately soluble in hot ligroïn. The best solvent for it is strong hot nitric acid or a mixture of benzol and ligroïn. Insoluble in strong hydrochloric acid whether cold or hot; insoluble in cold, soluble in hot nitric acid, or in sulphuric acid.

The parabromdimetanitrotoluol is a fairly reactive substance so far as the bromine which it contains is concerned. Cold ammonic hydrate has no action upon it, but a boiling solution of aqueous ammonic hydrate converts it into dinitro-

toluidine, which was recognized by its melting-point, 166°. When mixed with a cold solution of sodic hydrate, there is also no action, but, if the mixture is heated, the bromdinitrotoluol is slowly converted into the dinitrokresol melting at 85°. A boiling aqueous solution of sodic carbonate produces the same effect, but even more slowly. With sodic ethylate it gives a brilliant blue compound which, however, is very unstable. The behavior of other reagents, which led to new compounds, is described in some of the following sections of this paper.

Many attempts were made to introduce bromine into the side chain of the bromdinitrotoluol, but none led to the desired result. In fact the stability of this substance toward bromine is remarkable, as shown by the following experiment: Five grams of bromdinitrotoluol were heated with a large excess of bromine in a flask, with a return-condenser fitted to it by means of a plug of asbestos, to a temperature of 200°–210°, by means of an oil-bath, the contents of the flask being at the same time exposed to full sunlight. The heating was continued for five days, but in all this time no evolution of hydrobromic acid was observed, and at the end of the experiment almost the whole of the bromdinitrotoluol was recovered unaltered. The small amount which was acted on seemed to be completely decomposed, as no other compound could be isolated.

The same bromdinitrotoluol was also prepared from parabrommetanitrotoluol made from mononitrotoluidine (melting-point 114°) by Sandmeyer's reaction. For this purpose the bromnitrotoluol (which had not been brought into the solid state) was slowly added to about five times its weight of nitric acid of specific gravity 1.52, in which it dissolved easily and quietly. The solution was heated on the steam-bath for about ten minutes, and then poured into cold water. The white precipitate thus obtained after a somewhat tedious purification by crystallization from alcohol showed the constant melting-point 118°. The mother-liquors yielded a liquid which probably was unaltered bromnitrotoluol, but may have contained an isomeric dinitro compound. This method of preparing

bromdinitrotoluol is far inferior to that for making it from dinitrotoluidine.

Action of Aniline on Bromdinitrotoluol.

The bromdinitrotoluol was dissolved in an excess of aniline with the aid of a little heat, when a reaction took place, the product of which was obtained by removing the unaltered aniline and the aniline bromide formed with hydrochloric acid and water. The residue was then purified by crystallization from a mixture of benzol and alcohol, until it showed the constant melting-point 169°, when it was dried at ordinary temperatures and analyzed with the following result:

0.2000 gram of the substance gave 27.0 cc. of nitrogen at a temperature of 24° and a pressure of 759 mm.

	Calculated for $C_6H_3C_6H_5NH(NO_2)_2CH_3$.	Found.
Nitrogen	15.38	15.16

The substance is, therefore, paranilidodimetanitrotoluol, formed by replacing the atom of bromine by the anilido group. The yield was essentially quantitative.

Properties of Paranilidodimetanitrotoluol.— It crystallizes from a mixture of benzol and alcohol in long, very slender, much branched, orange needles. It melts at 169°. It is very soluble in chloroform or acetone; freely soluble in carbonic disulphide or ethyl acetate, much more soluble in the latter when hot; soluble in ether; slightly soluble in cold ethyl or methyl alcohol, in benzol, or in glacial acetic acid; more soluble in these three solvents when they are hot; almost insoluble in water or ligroïn. The best solvent for it is a mixture of benzol and alcohol. Strong nitric acid (sp. gr. 1.36) converts it into a yellow substance, probably a nitro compound; strong sulphuric acid dissolves it in the cold apparently without change. It is insoluble in an aqueous solution of sodic hydrate. With sodic ethylate it gives an unstable green compound.

An unsuccessful attempt was made to obtain the anilidodinitrotoluol described above by the action of dinitrotoluidine on aniline chloride according to the method used in getting diphenylamine from aniline and aniline chloride. For this

purpose 2.0 grams of dinitrotoluidine mixed with the chloride from 0.93 gram of aniline and 50 cc. of water were heated over night to 200°–210° in a sealed tube. Upon examining the contents of the tube no anilidodinitrotoluol could be detected. Most of the dinitrotoluidine was recovered unaltered, but part of it had been completely charred, apparently by the hydrochloric acid of the aniline chloride, as the aniline was found in the free state. This result makes it probable that no reaction of the sort desired takes place with these substances.

Nitrosoanilidodinitrotoluol, $C_6H_3C_6H_5NNO(NO_2)_2CH_3$.

This substance was prepared as follows: Five grams of anilidodinitrotoluol were mixed in a flask with 30 cc. of benzol and about 50 cc. of hydrochloric acid. Part of the substituted toluol dissolved in the benzol, and the rest remained suspended in this solution, which floated on the hydrochloric acid. Small pieces of sodic nitrite were then introduced from time to time into the mixture, which was kept well cooled throughout the process. The nitrous fumes in escaping through the benzol solution converted the anilido into the nitroso compound, all of which went into solution in the benzol, when the process was complete. The contents of the flask were then poured into a large beaker, diluted with water and freed from benzol by blowing a stream of air over the surface of the liquid. The solid residue deposited from the benzol sank to the bottom of the beaker, and was filtered out. As thus obtained it was practically pure, but for greater precaution it was crystallized from chloroform. It melted constant at 123°, and was analyzed with the following result:

0.2000 gram of the substance gave 32.42 cc. of nitrogen at a temperature of 19°.5 and a pressure of 762.5 mm.

	Calculated for $C_6H_3C_6H_5NNO(NO_2)_2CH_3$.	Found.
Nitrogen	18.54	18.58

The yield is essentially quantitative.

Properties of Nitrosoanilidodinitrotoluol.—Crystallized from chloroform it appears in good-sized rhombic plates, probably of the trimetric system. It is colorless to pale yellow. It melts at 123°, decomposing with evolution of much gas; this decomposition also takes place at lower temperatures, as the

substance blackens on account of it, if heated for a short time in the steam-bath, or if heated for a longer time to temperatures below 100°. It is very soluble in benzol, toluol, acetone, chloroform, or carbonic disulphide; freely soluble in glacial acetic acid or ethyl acetate; soluble in ethyl or methyl alcohol, or in ether; slightly soluble in ligroïn; essentially insoluble in water, whether hot or cold. The best solvent for it is cold chloroform. In crystallizing it, heating the solutions should be avoided, as this is apt to bring about decomposition. It gives no colored compound with sodic ethylate.

Bromdinitrotoluol and Sodium Malonic Ester.

A number of attempts were made to prepare a malonic ester derivative from the bromdinitrotoluol, but in no case with success. The action of the sodium malonic ester on the bromdinitrotoluol was tried at ordinary temperatures, at 0°, with a boiling solution of ethyl alcohol, with a boiling solution of amyl alcohol, but in all these cases nearly the whole of the bromdinitrotoluol was recovered unaltered. The only new product, when there was one, occurred in the shape of a tarry mass, amounting to a few per cent. of the total weight, which we ascribe to the action of a slight excess of the sodic ethylate used in making the sodium malonic ester. We infer, therefore, that sodium malonic ester does not act on bromdinitrotoluol, and this inference is confirmed by the fact that we saw no signs of one of the red salts so characteristic of the substituted malonic esters of this class.

Parabromdimetanitrobenzoic Acid, $C_6H_2Br(NO_2)_2COOH$.

In trying to oxidize the bromdinitrotoluol with nitric acid we found that it was entirely unaffected either by dilute nitric acid or the ordinary strong acid of sp. gr. 1.36 in open vessels. In fact we founded a method of purifying the bromdinitrotoluol on this property, as has been already stated. By heating the bromdinitrotoluol in a sealed tube with strong nitric acid, a mixture of bromdinitrobenzoic acid and the unaltered toluol was obtained, but this inconvenient method of oxidation was abandoned for the action of potassic dichromate and sulphuric acid. We proceeded, therefore, as fol-

lows: The bromdinitrotoluol was boiled for eight hours in a flask with a return-condenser with an excess of potassic dichromate and sulphuric acid diluted with an equal volume of water. If the oxidation was complete, colorless rhombic plates of the acid separated from the solution when it was allowed to cool slowly. These were filtered out on a platinum cone, washed free from sulphuric acid with a little water and dried, when they were found to be pure. The acid filtrate gave no precipitate on the addition of water. On one occasion a portion of the diluted filtrate was extracted with benzol, but the amount of acid obtained was so small that this extraction was not used again. If the oxidation of the bromdinitrotoluol had not taken place completely, as was sometimes the case, the unaltered substance which remained melted in the liquid during the boiling, solidified when the liquid cooled in lumps, which were easily picked out from the loose crystals of the acid. By treating these lumps with a cold solution of sodic carbonate, the bromdinitrobenzoic acid was converted into its sodium salt and dissolved. The unaltered bromdinitrotoluol was then filtered out, and the sodium salt purified by recrystallization. The pure acid as obtained directly from the oxidation melts at 181°. It was dried at 100° and analyzed with the following result:

0.1670 gram of the substance gave, by the method of Carius, 0.1081 gram of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2COOH$.	Found.
Bromine	27.50	27.54

The bromdinitrotoluol gave, by the process just described, about its own weight of the bromdinitrobenzoic acid, that is, about 90 per cent. of the theoretical yield.

Properties of Bromdinitrobenzoic Acid.—The substance crystallizes from dilute sulphuric acid in colorless rhombic plates or flat prisms. On evaporating a solution of the acid in alcohol to dryness on the water-bath a syrup was obtained, which on long standing deposited three monoclinic prisms, one of which was nearly 2 cm. long. Unfortunately a slight rise in temperature of the room caused these crystals to redissolve before they could be removed and their identity estab-

lished by a melting-point determination, and we have never succeeded in getting such crystals again. We feel little doubt, however, that these were crystals of the acid. It melts at 181°. It is very soluble in ethyl or methyl alcohol, in ether, ethyl acetate, or acetone; freely soluble in benzol, glacial acetic acid, or chloroform; moderately soluble in carbonic disulphide; slightly soluble in cold ligroïn, somewhat more soluble in hot; slightly soluble in water. The best solvent for it is a mixture of benzol and ligroïn. It is insoluble in hydrochloric acid whether cold or hot; insoluble in nitric or sulphuric acid in the cold, somewhat soluble in either when hot, and can be obtained unchanged from these solutions.

The bromdinitrobenzoic acid is a very reactive substance; a cold dilute solution of sodic hydrate dissolves it, forming the sodium salt described below, but, if the solution of the salt is allowed to stand some time in the cold with sodic hydrate, the atom of bromine is replaced by hydroxyl, and the disodium salt of the oxydinitrobenzoic acid melting at 245°–246° is formed. The same reaction takes place rapidly if the two reagents are heated together. Sodic carbonate in cold aqueous solution forms the salt of the bromdinitrobenzoic acid, but does not act further upon it. When sodic carbonate is heated with the acid, the disodic salt of the oxydinitrobenzoic acid is formed, as in the case of sodic hydrate. Ammonic hydrate in the cold forms the ammonium salt of bromdinitrobenzoic acid, but on standing with an excess of ammonic hydrate this is converted into ammonic chrysanisate by the replacement of the bromine by the amido group. This was proved by the melting-point, 259°, of the acid formed. Sodic ethylate gives with the bromdinitrobenzoic acid an intense reddish-purple color, which served as a very delicate and distinctive test for the presence of bromdinitrobenzoic acid.

Metaphenylenediamine gave an amidophenylimido compound, which was not further studied.

Sodic Bromdinitrobenzoate, $C_6H_2Br(NO_2)_2COONa.4H_2O$.—A quantity of bromdinitrobenzoic acid was mixed with a slight excess of sodic carbonate, hot water was added, and the

mixture warmed until the acid had dissolved. The heating was not continued longer than was absolutely necessary, as the salt decomposed when its solution was heated. As the hot solution cooled, crystals were deposited in large quantity, which were filtered out, and purified by one crystallization from water. The sodic bromide and sodic oxydinitrobenzoate formed by the decomposition of the bromdinitrobenzoic acid were contained principally in the mother-liquor from the first crystals. The substance separated by acidification from the mother-liquors of the second crystallization was essentially pure bromdinitrobenzoic acid. The salt was accordingly analyzed as follows:

I. 0.5874 gram of the air-dried salt lost 0.1097 gram of water when dried at 110°.

II. 0.4437 gram of air-dried salt lost 0.0832 gram of water when dried at 110°.

	Calculated for $C_6H_2Br(NO_2)_2COONa.4H_2O$.	Found. I.	II.
Water	18.70	18.68	18.75

I. 0.4777 gram of the salt dried at 110° gave 0.1053 gram of sodic sulphate.

II. 0.3605 gram of the salt dried at 110° gave 0.0800 gram of sodic sulphate.

	Calculated for $C_6H_2Br(NO_2)_2COONa$.	Found. I.	II.
Sodium	7.35	7.14	7.19

The sodic bromdinitrobenzoate crystallizes in fine needles, which are white with a faint tinge of straw-color. It is moderately soluble in cold water, very readily soluble in hot water. If the solution is heated for some time, sodic bromide and oxydinitrobenzoic acid are formed. A similar decomposition takes place more rapidly with an excess of alkali. In fact, with sodic hydrate this change will go on even in the cold.

Argentic Bromdinitrobenzoate, $C_6H_2Br(NO_2)_2COOAg$.—This substance was obtained from a solution of the ammonium salt made as follows: Some bromdinitrobenzoic acid was treated with ammonic hydrate in the proportion of 1 molecule of each substance. The ammonic hydrate solution was made so dilute that all the salt formed was in solution. To

this solution a concentrated solution of argentic nitrate was added, and the whole was thoroughly stirred, when a copious white precipitate made up of fine needles was thrown down. This was filtered out, washed with a little water, dissolved in dilute alcohol, filtered once more, and allowed to crystallize. The crystals thus obtained were dried by exposure to the air, and then heated to 100°, when they were found to suffer no loss of weight, and were accordingly analyzed with the following result:

0.1978 gram of the salt gave, by heating in a sealed tube with nitric acid and a crystal of potassic bromide, 0.0927 gram of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2COOAg$.	Found.
Silver	27.13	26.91

The silver salt crystallizes from dilute alcohol in bunches of dull gray needles. Just after it is formed it is very appreciably soluble in water, but it grows less soluble on standing, and after it has been dried is almost insoluble in water. When first precipitated the salt is white.

We also studied the behavior of an aqueous solution of sodic bromdinitrobenzoate with salts of all the common basic radicals. Of these only four produced precipitates including argentic nitrate, the action of which has just been described.

Ferric chloride gave a heavy white precipitate slightly soluble in cold, more soluble in hot water.

Plumbic acetate gave a precipitate similar to the preceding in appearance and solubility.

Cupric sulphate gave a light green precipitate, more soluble than the others.

Ethyl Ester of Bromdinitrobenzoic Acid, $C_6H_2Br(NO_2)_2COOC_2H_5$. —Five grams of bromdinitrobenzoic acid were dissolved in about 25 cc. of absolute alcohol and the solution was saturated with dry hydrochloric acid gas. During the saturation much of the ester was precipitated, as it is less soluble in alcohol than the acid. In order to complete the reaction the mixture was allowed to stand over night, and then poured into water, after which the precipitated ester was filtered out, and purified by crystallization from alcohol, until it showed

the constant melting-point, 105°, when it was dried and analyzed with the following result:

0.2227 gram of the substance gave, by the method of Carius, 0.1307 gram of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2COOC_2H_5$.	Found.
Bromine	25.08	24.96

Properties of the Bromdinitrobenzoic Ethyl Ester.—It crystallizes from alcohol in fine short white needles, which melt at 105°. It is very soluble in benzol, toluol, chloroform, acetone, or ethyl acetate; easily soluble in ether; moderately soluble in alcohol, carbonic disulphide, or glacial acetic acid, much more soluble in these solvents when they are hot; almost insoluble in cold ligroïn, slightly soluble in it when hot; insoluble in water. By crystallization from ordinary alcohol the ester is slowly converted into the corresponding acid. Cold sodic or ammonic hydrate in aqueous solution does not affect it, but either of these reagents when hot saponifies it, and the same effect is produced by hot dilute acids. An alcoholic solution of sodic ethylate gives an intense rose color with it, very similar to the color of eosine, but on standing this gradually changes to a reddish purple on account of the saponification of the ether.

Some experiments were tried with the purpose of preparing parabromdimetanitrobenzoic acid by Griess's reaction from chrysanisic acid. H. Salkowski states[1] that he was unable to obtain a diazo compound from chrysanisic acid in the cold, and we can confirm this observation, as in one experiment a mixture of chrysanisic acid (made by oxidation of dinitrotoluidine according to Frederici[2]) and hydrobromic acid was submitted to the action of nitrous anhydride for over two months, and no reaction could be observed. This negative result is the more conclusive, because we possessed in sodic ethylate a reagent by which even a trace of bromdinitrobenzoic acid could be detected with certainty. On the other hand, Salkowski[3] succeeded in making oxydinitrobenzoic acid from chrysanisic acid by acting on it with nitrous acid in

[1] Ann. Chem. (Liebig), **163**, 34. [2] Ber. d. chem. Ges., **11**, 1976.
[3] Ann. Chem. (Liebig), **163**, 36.

presence of boiling dilute acids, and accordingly we proceeded as follows: One gram of chrysanisic acid was mixed with a solution of hydrobromic acid of specific gravity 1.44, the mixture heated to boiling, and small pieces of sodic nitrite added from time to time. After about half an hour of this treatment all the chrysanisic acid had passed into solution, but that it had not been completely converted into bromdinitrobenzoic acid was shown by the strong yellow color of the liquid, which was not removed by further addition of sodic nitrite. The solution was now poured into cold water, and on standing a few faintly yellow crystals were deposited, which melted a little below the melting-point of bromdinitrobenzoic acid. The quantity was too small to raise the melting-point by crystallization, but we established its identity by the following tests. Some of the substance gave with an alcoholic solution of sodic ethylate the characteristic reddish purple color of the bromdinitrobenzoic acid. By treatment with aniline it was converted into orange-red needles, which melted at 235°–6°, instead of 239°, the melting-point of anilidodinitrobenzoic acid, and showed with sodic ethylate the pansy-purple color characteristic of it. This method of preparing bromdinitrobenzoic acid is inferior to that for making it from bromdinitrotoluol, since it gives a very small yield, and a tedious purification would be necessary to get rid of the unaltered chrysanisic acid.

Anilidodinitrobenzoic Acid, $C_6H_3C_6H_4NH(NO_2)_2COOH$.—This substance was prepared by warming some bromdinitrobenzoic acid with a slight excess of aniline. As soon as the acid had dissolved the mixture was allowed to cool, and, after removing the excess of aniline with hydrochloric acid and water, the residue was purified by crystallization from a mixture of benzol and alcohol until it showed the constant melting-point, 239°, when it was dried at 100° and analyzed with the following result:

0.2001 gram of the substance gave 23.7 cc. of nitrogen at a temperature of 15° and a pressure of 749 mm.

	Calculated for $C_6H_3C_6H_4NH(NO_2)_2COOH$.	Found.
Nitrogen	13.86	13.67

Properties of Anilidodinitrobenzoic Acid.—It crystallizes from a mixture of benzol and alcohol in orange needles or slender prisms, terminated by a single plane at an oblique angle. It melts at 239°. It is very soluble in ether, acetone, glacial acetic acid, or ethyl acetate; moderately soluble in cold chloroform, more soluble in hot; slightly soluble in benzol, or ethyl alcohol when cold, fairly soluble in either when hot; more soluble in methyl than in ethyl alcohol; slightly soluble in carbonic disulphide, or ligroïn; essentially insoluble in water. Cold hydrochloric acid or nitric acid does not dissolve it, but with hot nitric acid it goes into solution, and water precipitates what seems to be a new compound. It dissolves unchanged in cold sulphuric acid. Alkalies and alkaline carbonates dissolve it, forming salts. With a cold concentrated solution of sodic hydrate it gives a purple color similar to that of a dark pansy, which changes in a few minutes to a greenish-brown. Sodic ethylate gives the same color, which in this case is more permanent. When boiled with a strong solution of sodic hydrate aniline is set free, and the oxydinitrobenzoic acid, melting at 245°–246°, is formed. At the same time a considerable amount of phenylisocyanide is evolved.

Sodic Anilidodinitrobenzoate, $C_6H_3C_6H_3NH(NO_2)_2COONa.3H_2O$.—This salt was made by boiling the acid with an aqueous solution of an excess of sodic carbonate, until it had dissolved, which took several hours. The solution was then concentrated, when, upon cooling, it deposited crystals of the salt, which were purified by recrystallization from water, after which it was analyzed with the following results:

I. 0.5867 gram of the air-dried salt when dried at 100° lost 0.0828 gram of water.

II. 0.3487 gram of the salt dried in air lost when dried *in vacuo*, over sulphuric acid, 0.0493 gram of water.

	Calculated for $C_6H_3C_6H_3NH(NO_2)_2COONa.3H_2O$.	Found. I.	II.
Water	14.25	14.11	14.14

The substance, therefore, contains 3 molecules of water of crystallization, which it loses *in vacuo*.

I. 0.2104 gram of the salt dried at 100° gave 0.0460 gram of sodic sulphate.

II. 0.2998 gram of the salt dried at 100° gave 0.0653 gram of sodic sulphate.

	Calculated for $C_6H_3C_6H_3NH(NO_2)_2COONa$.	Found. I.	II.
Sodium	7.08	7.08	7.06

The salt forms orange-red needles and is freely soluble in water.

Calcic Anilidodinitrobenzoate, $(C_6H_3C_6H_3NH(NO_2)_2COO)_2Ca.7H_2O$.—This salt was made by boiling the acid with calcic carbonate and water for two days. At the end of this time the solution of the salt was filtered off from the excess of calcic carbonate and a little unaltered acid. The filtrate was then concentrated and set aside to crystallize, when the crystals were analyzed with the following results:

I. 0.4050 gram of the air-dried salt, when dried at 100°, lost 0.0359 gram of water.

II. 0.2991 gram of the air-dried salt, when dried at 100°, lost 0.0264 gram of water.

	Calculated for $(C_6H_3C_6H_3NH(NO_2)_2COO)_2Ca.7H_2O$.	Found. I.	II.
Water	8.91	8.86	8.83

I. 0.3691 gram of the salt, dried at 100°, gave 0.0773 gram of calcic sulphate.

II. 0.2727 gram of the salt, dried at 100°, gave 0.0572 gram of calcic sulphate.

	Calculated for $(C_6H_3C_6H_3NH(NO_2)_2COO)_2Ca$.	Found. I.	II.
Calcium	6.21	6.16	6.17

The salt when dried *in vacuo* over sulphuric acid loses only two of its molecules of water of crystallization, as is shown by the following results, although a larger amount seems to be given off very slowly:

I. 0.4050 gram of the air-dried salt lost *in vacuo* 0.0114 gram of water.

II. 0.2991 gram of the air-dried salt lost *in vacuo* 0.0088 gram of water.

	Calculated for $(C_6H_3C_6H_4NH(NO_2)_2COO)_2Ca.7H_2O$.	Found I.	Found II.
$2H_2O$	2.55	2.81	2.94

The salt resembles the sodium salt except that the reddish-orange needles which it forms are shorter. It is readily soluble in water.

A solution of the sodium salt gave the following precipitates with salts of the common metals:

Argentic nitrate gave a precipitate of reddish-orange needles insoluble in cold or hot water.

Cupric sulphate gave a yellow precipitate, insoluble in cold water, slightly soluble in hot.

Ferric chloride or *manganous chloride* gave a precipitate consisting of orange needles slightly soluble in cold water, moderately soluble in hot.

Nickelous chloride gave a yellow precipitate, moderately soluble in cold, freely soluble in hot water.

Cadmic sulphate, *zincic sulphate*, *baric chloride*, or *strontic chloride* gave an orange precipitate, moderately soluble in cold, readily soluble in hot water.

Magnesic sulphate gave no precipitate, but, on standing, a large number of red needles arranged in radiating groups were deposited, which were readily soluble even in cold water.

Anilidodinitrobenzoic Ethyl Ester, $C_6H_3C_6H_4NH(NO_2)_2COOC_2H_5$.—The acid mixed with an amount of absolute alcohol, in which it only partially dissolved, was saturated with dry hydrochloric acid gas, and then heated for a short time on the steam-bath. The liquid was then allowed to cool, and the undissolved portion filtered out. This proved to be nearly pure ester, and was easily purified by crystallization from alcohol. An additional amount of the ester was obtained by diluting the filtrate, and purified by crystallization from a mixture of benzol and alcohol. The pure ester showed the constant melting-point, 154°. It was dried and analyzed with the following result:

0.1926 gram of the substance gave, on combustion, 0.3842 gram of carbonic dioxide and 0.0700 gram of water.

	Calculated for $C_6H_3C_6H_4NH(NO_2)_2COOC_2H_5$.	Found.
Carbon	54.39	54.40
Hydrogen	3.93	4.04

Two grams of anilidodinitrobenzoic acid gave 2.1 grams of the ester instead of the 2.19 grams required by theory; the yield therefore amounted to 96 per cent.

Properties of Anilidodinitrobenzoic Ethyl Ester—It crystallizes from a mixture of benzol and alcohol in thin plates or long prisms, apparently of the monoclinic system and having a bright orange color. It melts at 154°. It is very soluble in chloroform; freely soluble in benzol, or acetone; soluble in ether, carbonic disulphide, glacial acetic acid, or ethyl acetate; slightly soluble in ethyl or methyl alcohol, or ligroïn, its solubility in these solvents being increased somewhat by heat. The best solvent for it is a mixture of benzol and alcohol in the proportion of 1 to 2. Cold dilute acids or alkalies do not dissolve it, but it is saponified by them when hot. Sodic ethylate gives a cherry-red color, but this color is not produced by aqueous sodic hydrate.

Nitrous Acid and Anilidodinitrobenzoic Acid.

In the hope of preparing a nitroso compound, 1 gram of anilidodinitrobenzoic acid dissolved in 25 grams of pure benzol was mixed with 100 cc. of dilute hydrochloric acid, and to the well-cooled mixture small pieces of sodic nitrite were added from time to time, the experiment being carried on in the same way as that for making the corresponding toluol compound. After this treatment had been continued a long time the benzol was evaporated with a stream of air, when the 1 gram of the acid was recovered unaltered. If, therefore, the nitroso compound of the acid can be formed at all, its formation is much more difficult than that of the corresponding toluol compound.

Action of Sodium Malonic Ester on Bromdinitrobenzoic Acid.—Formation of Dinitrocarboxylphenylmalonic Ester,

$$C_6H_3CH(COOC_2H_5)_2(NO_2)_2COOH.$$

Five grams of bromdinitrobenzoic acid dissolved in about 30 cc. of absolute alcohol were treated with 5 grams of malonic ester previously converted into the sodium compound

by the addition of an alcoholic solution of the sodic ethylate made from 1.5 grams of sodium. This gives the proportion of a little less than 2 molecules of malonic ester to each molecule of the bromdinitrobenzoic acid. A strong dark-red color appeared as soon as the substances were mixed, but to be certain that the reaction was complete, the mixture was allowed to stand at the ordinary temperature over night. Under these conditions a precipitate was formed consisting partly of sodic bromide, and partly of bunches of red crystals of the sodium salt of the new compound. Disregarding this precipitate, water and dilute sulphuric acid were added, which decolorized the solution, and precipitated a yellowish oil. This was separated from the aqueous liquid and allowed to stand, when it solidified in a short time, and was then purified by crystallization from alcohol until it showed the constant melting-point, 176°, when it was dried at 100°, and analyzed with the following results:

I. 0.2282 gram of the substance gave, on combustion, 0.3783 gram carbonic dioxide and 0.0960 gram of water.

II. 0.2237 gram of the substance gave 15.8 cc. of nitrogen at a temperature of 25°.5 and a pressure of 765 mm.

	Calculated for $C_6H_2CH(COOC_2H_5)_2(NO_2)_2COOH$.	Found. I.	II.
Carbon	45.40	45.23	....
Hydrogen	3.78	4.67	....
Nitrogen	7.57	....	7.88

Five grams of the bromdinitrobenzoic acid gave 4.5 grams of the carboxyldinitrophenylmalonic ester instead of the 6.4 grams calculated from the formulas, that is, a yield of 70 per cent.

The formation of this substance from the bromdinitrobenzoic acid takes place with great ease, as it was found that a mixture of the brom acid, malonic ester, and alcohol, if treated with dilute aqueous sodic hydrate, was at once colored deep red by the formation of the sodium salt of the carboxydinitrophenylmalonic ester, and upon acidifying this red solution with dilute sulphuric acid a precipitate of the free ester was obtained, while sodic bromide could be detected in the filtrate. In none of this work was any dinitrobenzoic acid de-

tected, which might have been formed by the replacement of the bromine by hydrogen, as happens in the corresponding reaction with tribromdinitrobenzol.

Properties of Carboxydinitrophenylmalonic Ester, $C_6H_3CH(COOC_2H_5)_2(NO_2)_2COOH$.—It crystallizes from alcohol in short, thick, white prisms terminated by a plane at an oblique angle. It melts at 176°. It is very soluble in acetone; readily soluble in ethyl acetate; moderately soluble in cold ethyl or methyl alcohol, ether, or glacial acetic acid, readily soluble in each of these liquids if hot; moderately soluble in benzol, chloroform, or carbonic disulphide; essentially insoluble in water or in cold ligroïn, and slightly soluble in hot ligroïn. The best solvent for it is alcohol. Dilute acids in the cold have no effect upon it. It dissolves in aqueous solutions of the alkalies or alkaline carbonates forming the dark-red salts. It behaves like a dibasic acid.

Silver Ammonium Salt of Carboxydinitrophenylmalonic Ester.—A weighed amount of the carboxydinitrophenylmalonic ester was dissolved in water which contained 2 molecules of ammonic hydrate for each molecule of the ester, and, after filtering, a solution of argentic nitrate was added to it slowly with constant stirring. A precipitate was formed at once, and, after an excess of argentic nitrate had been added, and the whole thoroughly stirred, the red color of the ammonium salt almost entirely disappeared. The heavy, white precipitate was filtered out and thoroughly washed with water, although it dissolved in it to an appreciable extent. The salt was dried in the air, as it was found to be decomposed if heated to 100°, forming at first a reddish and afterward a black amorphous mass. This precipitated salt was used in Analyses II. and III. In one preparation the wash waters were allowed to run into the filtrate, which contained a large excess of argentic nitrate. On standing over night white crystals were deposited, which were filtered out, washed, and dried at ordinary temperatures. They proved identical with the salt formed by direct precipitation, as shown by the following analyses, since in I. these crystals were used:

I. 0.1114 gram of the crystallized salt gave, by heating

with nitric acid and a crystal of potassic bromide in a sealed tube, 0.0426 gram of argentic bromide.

II. 0.1213 gram of the precipitated salt gave 0.0463 gram of argentic bromide.

III. 0.1006 gram of the precipitated salt gave 0.0383 gram of argentic bromide.

	Calculated for $C_6H_3CAg(COOC_2H_5)_2(NO_2)_2COONH_4$.	Found. I.	II.	III.
Silver	21.86	21.97	21.93	21.87

These analyses indicate that the salt is an ammonio-silver salt, instead of the disilver salt which we had expected. The relative position of the silver and ammonium in the molecule was not determined. We have put the silver provisionally in the malonic ester group in the formula given above, because the salt is white, whereas the ammonium compound from which it is formed is red, and in other cases we have found that the presence of a basic radical, such as sodium or ammonium, in this group gives rise to red salts; it seems more probable, therefore, that the ammonium has replaced hydrogen in the carboxyl rather than in the malonic ester group.

The salt forms a heavy, white precipitate or white crystals; it is slightly soluble in water and decomposed by heating it to 100°.

Action of Metaphenylene Diamine on Parabromdimetanitrotoluol. Formation of Metamidophenylenimidodinitrotoluol,

$$NH_2C_6H_4NHC_6H_2(NO_2)_2CH_3.$$

This work was undertaken in the hope of obtaining molecules consisting of long chains of phenyl and phenylene rings in order to study the effect of the increasing complexity of the molecules upon the properties of the substances. As explained in the introduction we were unable to carry out our plan, but give here the description of the preparation and properties of the new compounds obtained.

Metaphenylenediamine acts on bromdinitrotoluol with such violence, that, if the substances are mixed without a diluent, enough heat is given off to volatilize a large part of the metaphenylenediamine in dense white clouds, while there is left a black, amorphous, charred mass from which only a very small amount of substance can be extracted. We accord-

ingly mixed the two substances with about three times their volume of alcohol, and, after warming gently for a short time, allowed the alcohol to evaporate spontaneously. The residue was then dissolved in hot hydrochloric acid, and after filtration rendered alkaline with sodic carbonate. This threw down a red precipitate, almost insoluble in water, which was filtered out, washed, dried, and purified by crystallization from a mixture of benzol and alcohol, until it showed the constant melting-point, 185°, when it was dried at 100°, and analyzed with the following results:

I. 0.2039 gram of the substance gave 36.1 cc. of nitrogen at a temperature of 22° and a pressure of 758 mm.

II. 0.1997 gram of the substance gave 33.3 cc. of nitrogen at a temperature of 15° and a pressure of 763 mm.

	Calculated for $NH_2C_6H_4NHC_6H_2(NO_2)_3CH_3$.	Found. I.	II.
Nitrogen	19.45	19.92	19.56

Only 1 molecule of the bromdinitrotoluol therefore had reacted with the phenylenediamine.

Properties of Amidophenylenimidodinitrotoluol ($CH_3.1.NO_2.3.NH4.NO_2.5$).—Crystallized from benzol and alcohol it forms rather stout, blunt prisms arranged in fan-shaped groups. These prisms are a vivid reddish-brown with a very marked, yellowish-green reflex. From benzol alone it crystallizes in dark red lancet-shaped blades. It melts at 185°. It is very soluble in acetone; freely soluble in methyl alcohol, benzol, chloroform, glacial acetic acid, or ethyl acetate; moderately soluble in ether, carbonic disulphide, or cold ethyl alcohol; more soluble in hot alcohol; almost insoluble in ligroïn or water. The best solvent for it is a mixture of alcohol and benzol. Hydrochloric acid or sulphuric acid forms with it a dark oily mass, probably a salt, as it dissolves in a large quantity of water, and solutions of the alkalies or alkaline carbonates precipitate the unaltered substance from this solution. Nitric acid of specific gravity 1.36 dissolves it forming a yellow solution, from which water precipitates a new yellow body, probably a nitro compound. Cold solutions of alkalies or alkaline carbonates have no action on it, but alkaline solutions when hot decompose it. Sodic ethylate gives with it a green

color, very similar to that obtained from anilidodinitrotoluol. It was not converted into an acetyl compound even by boiling for three hours with glacial acetic acid, the original substance being recovered unaltered.

An attempt was made to obtain a reaction between amidophenylenimidodinitrotoluol and bromdinitrotoluol. For this purpose the two substances were mixed in the proportion of equal molecules, heated until they melted, and kept at this temperature for several minutes. No evolution of hydrobromic acid was observed, and on treating the cold mass with water no hydrobromic acid could be detected in the aqueous extract. The product was dissolved in alcohol, and the solution allowed to evaporate spontaneously, when the red lancet-shaped crystals of the amidophenylenimidodinitrotoluol were observed side by side with the slender white needles of the bromdinitrotoluol. It seems, therefore, that the two bodies do not react on each other, and that only one of the amido groups of the metaphenylenediamine can be affected by bromdinitrotoluol.

Many attempts were made to replace the amido group in amidophenylenimidodinitrotoluol with bromine by means of the diazo reaction, but none of them were successful, black, tarry masses being obtained in each case. The experiment was tried with strong hydrobromic acid and an excess of sodic nitrite; with just the calculated amount of sodic nitrite to form the diazo compound, as we thought the bad result might be due to the formation and decomposition of a nitroso compound from the imido group; in acetic acid solution; by Sandmeyer's reaction; and finally an attempt was made to prepare the diazo perbromide, but the bromine instead acted on the phenylene ring forming a tribrom compound.

Tribromamidophenylenimidodinitrotoluol,

$$NH_2C_6HBr_2NHC_6H_2(NO_2)_2CH_3.$$

This substance was prepared by treating amidophenylenimidodinitrotoluol with bromine water, which converted it into a yellow substance. When the red color of the original body was entirely changed to yellow, the product was filtered out, and purified by crystallization from boiling benzol, until it

showed the constant melting-point 222°, when it was dried at 100°, and analyzed with the following result:

0.1445 gram of the substance gave by the method of Carius 0.1552 gram of argentic bromide.

	Calculated for $NH_2C_6HBr_2NHC_6H_2(NO_2)_2CH_3$.	Found.
Bromine	45.71	45.70

The amidophenylenimidodinitrotoluol has therefore taken up three atoms of bromine in place of three of hydrogen, and it is probable that these atoms of bromine are attached to the benzol ring of the amidophenylenimido group. One gram of the original substance gave 1.8 grams of the tribrom compound instead o; the 1.82 grams required by theory. The yield is, therefore, 99 per cent.

Properties of Tribromamidophenylenimidodinitrotoluol.—The substance crystallizes from boiling benzol in rhombic plates of a brownish-yellow color, which melt at 222°. It is easily soluble in acetone; moderately soluble in benzol, chloroform, carbonic disulphide, or ethyl acetate; slightly soluble in methyl alcohol, ether, or glacial acetic acid; almost insoluble in ethyl alcohol, or ligroïn; insoluble in water. Boiling benzol is the best solvent for it. It is slightly soluble in strong hydrochloric acid or nitric acid; fuming nitric acid dissolves it more easily, and water precipitates from this solution a light yellow substance, perhaps a nitro-compound; it is soluble in strong sulphuric acid. Solutions of alkalies produce no effect on it in the cold. When warmed with alkalies, a reaction takes place producing a black solution, from which we did not succeed in isolating a pure substance. We had hoped by this decomposition of the body to determine the position of the atoms of bromine, but, as one of the products of the reaction was bromide of sodium, this was impossible. Sodic ethylate gives a bluish-violet color with it. Aniline had no effect upon it.

Tribromanilidodinitrotoluol, $C_6H_3Br_2NHC_6H_2(NO_2)_2CH_3$.

This substance was prepared in the course of the work on complex molecules mentioned in the introduction to this paper. Bromine water does not act easily upon the anilido-

dinitrotoluol, which, in this respect, differs from the corresponding amidophenylenimido body, whose behavior was described above. It was necessary, therefore, to use pure bromine, some of which was poured into an evaporating dish, and anilidodinitrotoluol added in small amounts at a time. The action was violent, the substance dissolving, and fumes of hydrobromic acid being given off. Enough bromine should be taken to moisten thoroughly all the solid used. The excess of bromine was evaporated off, the solid residue broken up and washed with cold alcohol, in which it is almost insoluble. The yellow powder thus obtained was recrystallized from boiling benzol until it showed the constant melting-point, 238°, when it was dried at 100°, and analyzed with the following result:

0.1918 gram of the substance gave, by the method of Carius, 0.2107 gram of argentic bromide.

	Calculated for $C_6H_2Br_2NHC_6H_2(NO_2)_2CH_3$.	Found.
Bromine	47.05	46.75

Properties of Tribromanilidodinitrotoluol.—It crystallizes from boiling benzol in yellow rhombic plates often with the acute angles truncated, which melt at 238°. It is soluble in chloroform or carbonic disulphide; moderately soluble in benzol, acetone, or ethyl acetate; slightly soluble in ether or glacial acetic acid; almost insoluble in ethyl or methyl alcohol, or in ligroïn; insoluble in water. Benzol is the best solvent for it. It is insoluble in either of the three strong acids, but dissolves in fuming nitric acid. A solution of sodic hydrate has no action on the substance, even if boiled with it for several minutes.

In the course of the work on complex molecules outlined in the introduction, an attempt was made to convert the substance just described into a nitro compound. For this purpose the tribromanilidodinitrotoluol was mixed with nitric acid of specific gravity 1.5, in which it dissolved without evolution of nitrous fumes forming a red solution. Cold water separated from this solution a precipitate resembling red sulphide of antimony in appearance, which was washed with water and dried. All our attempts to obtain a crystal-

line body from this precipitate have failed. It dissolved in several of the organic solvents, but these solutions left on evaporation a red viscous or resinous substance, which showed no signs of crystallization, even after long standing.

We next heated this product with aniline in the hope of getting a more manageable anilido compound. An anilido compound was produced, as shown by the formation of aniline bromide, and this proved that the uncrystallizable substance was a nitro compound, since the tribromanilidodinitrotoluol, from which it was made, did not give up bromine to aniline. This new anilido compound, however, behaved with solvents in the same unsatisfactory manner as the nitro compound, from which it was derived. Nor did a bromine derivative which was formed from this new anilido compound by the action of bromine, as indicated by the evolution of hydrobromic acid, show any signs of crystallization. As none of these derivatives could be brought into a state fit for analysis, we were obliged to give up this branch of the work.

Action of Pyridine on Bromdinitrobenzoic Acid.

If bromdinitrobenzoic acid is added to pyridine it gives a white crystalline precipitate, which almost immediately dissolves with evolution of heat, and from this new solution a heavy yellow precipitate is thrown down. To isolate the two products, which seemed to be formed by this action, we dissolved some bromdinitrobenzoic acid in absolute alcohol, and added to it an excess of pyridine, when white needles separated in large quantity. These were filtered out, washed with absolute alcohol, in which they were not very soluble, and then analyzed, but the result obtained did not correspond to any formula. It seemed to indicate rather that the substance was a mixture of the pyridine salt of bromdinitrobenzoic acid and the free acid; and this, as a matter of fact, is what we should have obtained, if the original crystals had been this pyridine salt, as they lost pyridine with great ease, when treated with alcohol. Although the analysis did not settle the composition of the crystals, the following facts leave little doubt that they were the salt

$$C_6H_2Br(NO_2)_2COOHC_5H_5N.$$

They showed the solubility of a salt, being slightly soluble in cold and freely soluble in hot water; sodic hydrate set free pyridine, and acids precipitated bromdinitrobenzoic acid from a solution of them. The solution gave no test for a bromide. Sodic ethylate gave the same reddish-purple color, which it gives with salts of bromdinitrobenzoic acid. We may add that the crystals were moderately soluble in cold, easily soluble in hot alcohol, and that with an excess of pyridine they passed easily into the yellow product obtained direct from pyridine and the acid.

The yellow product was prepared by evaporating the mother-liquor from the white salt, which still contained some of the crystals, or even by allowing it to stand at ordinary temperatures. We did not attempt to analyze this substance, as it is decomposed even by crystallization from alcohol, but we have been able to draw a safe inference in regard to its nature from its decomposition-products and its properties. As first prepared, it melted with decomposition at about 210°, but, if it was recrystallized from alcohol, some bromide of pyridine was eliminated, and the crystals showed a higher melting-point. By continuing the crystallization often enough all the bromine and pyridine were removed as bromide of pyridine, and the crystals melted constant at 245°–246°, and contained no bromine. This same substance could be obtained from the yellow substance by treating it with dilute sulphuric acid. After recrystallization from alcohol it appeared in elongated hexagonal plates of a light straw color. To determine the nature of this substance, it was converted into its calcium salt by warming it with calcic carbonate and water. The solution thus obtained was filtered, and upon concentration deposited yellowish-orange, well defined octahedra of the salt, which, after it had been crystallized, redissolved with great difficulty. The crystals were filtered out, pressed between filter paper, dried in the air, and analyzed with the results given under I. The filtrate, on further concentration, gave another crop of crystals, which were dried in the same way, and analyzed with the results given under II. The mother-liquor from these second crystals, when acidified, gave the acid with its proper melting-point, 245°–246°.

I. 0.2552 gram of the air-dried salt lost 0.0304 gram of water when heated to 157°.

II. 0.5226 gram of the air-dried salt lost 0.0602 gram of water at 160°.

	Calculated for $CaOCOOC_6H_3(NO_2)_2.2H_2O$.	Found. I.	II.
Water	11.92	11.92	11.52.

I. 0.2248 gram of the salt dried at 157° gave 0.1122 gram of calcic sulphate.

II. 0.4624 gram of the salt dried at 160° gave 0.2269 gram of calcic sulphate.

	Calculated for $CaOCOOC_6H_3(NO_2)_2$.	Found. I.	II.
Calcium	15.04	14.69	14.44

These results leave no doubt that the substance is the calcium salt of oxydinitrobenzoic acid, but the melting-point of this acid, 245°–246°, did not agree with that given by H. Salkowski[1] for paroxydimetanitrobenzoic acid which was 235°–237°. We accordingly made a careful study of the melting-point of this acid, which is described in a later section, and proved that its true melting-point is 245°–246°.

The work just described shows that the yellow pyridine compound is broken up by crystallization from alcohol, or by dilute sulphuric acid, into oxydinitrobenzoic acid and bromide of pyridine. That it was not a mixture of these two substances was shown by the fact that it took several crystallizations to remove all the pyridine and bromine, whereas bromide of pyridine is so soluble in alcohol that the whole of it would have been removed by the first crystallization, if it had existed already formed. That the substance is a salt is made probable by its solubilities, as it is slightly soluble in cold, freely soluble in hot water; slightly soluble in cold, moderately soluble in hot alcohol; insoluble in benzol or ether; and this view is confirmed by the facts that alkalies set free pyridine from its solutions, and argentic nitrate forms a red salt when added to the neutral solution. With an acidified solution it gives a precipitate of argentic bromide, but this may come from the bromide of pyridine formed by the acid, rather than

[1] Ann. Chem. (Liebig), 163, 36.

from the original yellow substance. The only formula which we have found that explains all these observations is

$$C_5H_5NBrC_6H_2(NO_2)_2COOHC_5H_5N,$$

derived from two molecules of pyridine and one of the brom-dinitrobenzoic acid. On this theory one of the molecules of pyridine is attached to the carboxyl group, while the other is attached to the bromine atom and the benzol ring of the substituted benzoic acid, forming a salt analogous to bromide of pyridine, as shown by the following formulas:

$$(C_5H_5N)Br(C_6H_2(NO_2)_2COOHC_5H_5N). \quad (C_5H_5N)BrH.$$

The decomposition of the yellow substance would then be represented by the following reaction:

$$C_5H_5NBrC_6H_2(NO_2)_2COOHC_5H_5N + H_2O = C_5H_5NBrH + HOC_6H_2(NO_2)_2COOH + C_5H_5N.$$

The Melting-Point of Paroxydimetanitrobenzoic Acid.—The acid obtained from the yellow pyridine compound by the action of dilute sulphuric acid or by crystallizing it from alcohol, as described in the preceding paragraph, melted at 245°–246°, which was also the melting-point of the oxydinitrobenzoic acid prepared by us by the action of sodic hydrate on brom-dinitrobenzoic acid. All these acids must be paroxydimeta-nitrobenzoic acid, and, as H. Salkowski[1] ascribes the lower melting-point, 235°–237°, to this body, we have felt it necessary to prepare this acid by the two methods given by him in order to remove this discrepancy. Accordingly, some chrysanisic acid was made by the method of Frederici,[2] the oxidation of dinitrotoluidine melting at 166°, with potassic dichromate and sulphuric acid. This melted at 259°. It was treated with sodic nitrite in a boiling, weak acid solution, until all the chrysanisic acid had been transformed into the new body. This took place very slowly. The product melted at the temperature stated by Salkowski, 235°–237°, with decomposition and blackening, but, after repeated crystallization from alcohol, the melting-point rose to 245°, and the signs of decomposition during melting vanished.

In order to apply Salkowski's second method some chrysanisic acid was heated with a dilute solution of sodic hydrate.

[1] Ann. Chem. (Liebig), **163**, 36.
[2] Ber. d. chem. Ges., **11**, 1975.

The mixture became dark-colored, and ammonia was given off. The liquid was evaporated to dryness on the steam-bath, the residue taken up with a little hot water, filtered, and precipitated with hydrochloric acid; this yielded a crude product, melting a little above 240°, which was raised to the constant melting-point, 245°, by crystallization from alcohol. If the heating of the chrysanisic acid was continued for a long time with a strong alkaline solution, upon acidification of the liquid no oxydinitrobenzoic acid was deposited, but there was a vigorous evolution of hydrocyanic acid. This behavior is analogous to that of the anilidodinitrobenzoic acid described earlier, which gives aniline and oxydinitrobenzoic acid at first with sodic hydrate, but by more vigorous treatment phenyl isocyanide. It also recalls the work of Wöhler[1] and of Post and Hübner[2] on the formation of cyanides by the action of alkaline hydrates in aqueous solution on aromatic nitro compounds.

The work just described shows that paroxydimetanitrobenzoic acid prepared in four different ways had the constant melting-point 245°–246°, and, therefore, that the melting-point 235°–237° ascribed to it by H. Salkowski rests probably on an error of observation. We should add that the thermometer used in this work was tested by determining the boiling-point of aniline and naphthalene with it. Aniline with the column in the vapor and at a pressure of 760 mm. showed the boiling-point 184°. Naphthalene under the same conditions gave a temperature of 218°–219°. There can be no doubt, therefore, that the thermometer was accurate enough for this work.

Chlordinitrobenzoic Acid.

The following work on the chlor compound could not be finished so thoroughly as we wished, because of the pressure of other parts of the research, but we have decided to describe our observations even in this imperfect state, since they seem to leave no doubt in regard to the nature of the substance obtained.

A quantity of chrysanisic acid was mixed with cold, strong hydrochloric acid, and treated with an excess of sodic nitrite.

[1] Pogg. Ann. **13**, 488, (1828).
[2] Ber. d. chem. Ges., **5**, 408, (1872).

To the mixture was then added a solution of cuprous chloride in strong hydrochloric acid, and the whole heated for about half an hour with occasional addition of more sodic nitrite. After the liquid had been cooled by the addition of water the product, a reddish, viscous mass, was removed by winding it about a rod, and was then sucked out as completely as possible with a filter pump. The residue was pressed between filter paper, and recrystallized from alcohol, and later from benzol, which is much more efficient in removing the tarry matter. In this way a crystalline body was obtained, the melting-point of which we did not succeed in raising above 159°, but we do not feel certain that the true melting-point may not lie a few degrees above this temperature, as our work was done with an insufficient amount of material, the yield being exceedingly small. For this reason also we were unable to analyze the substance, but the following observations show without doubt that it is chlordinitrobenzoic acid. It is insoluble in water or acids, but dissolves easily in alkalies or alkaline carbonates. It dissolves in aniline with the aid of heat, forming aniline chloride, and an orange-red acid, melting when not perfectly pure at 235°–238°; anilidodinitrobenzoic acid melts at 239°. This product also gave the pansy-purple color with sodic ethylate, which is characteristic of anilidodinitrobenzoic acid, whereas the chlor acid, melting at 159°, gives with sodic ethylate a reddish-purple color, closely resembling that obtained from bromdinitrobenzoic acid. With ammonic hydrate the acid, melting at 159°, gave ammonic chloride and a substance resembling chrysanisic acid in appearance, and melting in the crude state not far from the melting-point of this acid.

Properties of Chlordinitrobenzoic Acid.—It crystallizes in white, rather ill-defined, prisms, which probably melt at 159°. It is very soluble in ether or acetone; easily soluble in methyl alcohol, glacial acetic acid, or ethyl acetate; moderately soluble in ethyl alcohol, benzol, chloroform, or carbonic disulphide; almost insoluble in ligroïn. Benzol is the best solvent for it.

Action of Hydrochloric Acid on Bromdinitrobenzoic Acid.

These experiments, like those described in the preceding section, are unfinished, as it was intended to make this work the starting-point for a new research and, therefore, the study of the most interesting product of the reaction has been postponed until that could be undertaken. Bromdinitrobenzoic acid in quantities of two grams at a time was heated with fifteen cc. of hydrochloric acid, containing 11 per cent. of the acid, to 200° for five hours in a sealed tube. At the end of this time, it was found that the undissolved portion had collected into a liquid globule. The whole contents of the tube were poured into an evaporating dish, and allowed to stand, until the globule had solidified, and crystals had separated from the supernatant liquid. As these crystals gave with sodic ethylate the characteristic reddish-purple color of bromdinitrobenzoic acid, they were heated with a dilute solution of sodic carbonate on the steam-bath until no more dissolved. The residue melted after one recrystallization from alcohol at 119°, and was probably vicinal bromdinitrobenzol, although this supposition needs confirmation by analysis before it is accepted. The dark-red solution obtained by sodic carbonate gave, when acidified, a precipitate, which, by crystallization from alcohol, was separated into two substances. One of these melted at 245°, and was, therefore, oxydinitrobenzoic acid, formed by the action of the solution of sodic carbonate upon the bromdinitrobenzoic acid, although possibly some of it was one of the direct products of the reaction. The other substance melted at 62°, and we, therefore, inferred that it was the vicinal dinitrophenol ($OH.1.NO_2.2.NO_2.6.$) as this melts at 61°.78 according to Mills,[1] whereas its melting-point is given usually as 63°–64°. To confirm this view, we oxidized the substance with nitric acid, which converted it into picric acid, recognized by its melting-point 121°, its copper and lead salts, and the deep red color produced when it was heated with potassic cyanide. The formation of the dinitrophenol was to be expected, as Salkowski and Rudolph[2] have found that oxydinitrobenzoic acid, if heated with water to

[1] Phil. Mag. [5], 14, 27.

[2] Ber. d. chem. Ges., 10, 1255.

170° is converted into this vicinal dinitrophenol. The products of the action of hydrochloric acid at 200° on bromdinitrobenzoic acid would seem to be the following: Bromdinitrobenzol (?) (Br.1.NO_2.2.NO_2.6.) about one-fourth of the product; dinitrophenol of the same series, about one-third of the remainder; and unaltered bromdinitrobenzoic acid mixed perhaps with some oxydinitrobenzoic acid.

ALUMINUM ETHYLATE.[1]

By H. W. Hillyer and O. E. Crooker.

In our preliminary notice, which appeared in this Journal under the head of "Aluminum Alcoholates,"[2] mention was made of our investigation, as then incomplete, of the action of alcoholic solutions of anhydrous chlorides upon aluminum. That part of the work wherein ethyl alcohol was used has been completed, and the results as obtained are given in this article.

In their work on aluminum alcohols,[3] Gladstone and Tribe have prepared, by means of their aluminum-iodine reaction, several aluminum alcoholates, among which was the ethylate. Their method of procedure was as follows: by bringing together 2 grams of aluminum foil, 1 gram of iodine, and 20 cc. of absolute alcohol the elements were found to combine quickly and to produce the aluminum iodide necessary for the reaction, whereupon the decomposition of the alcohol began before the whole of the free iodine had passed into combination. The action proceeded with moderate rapidity until the metal had disappeared and the evolution of hydrogen ceased. The reaction was supposed to take place through the intervention of intermediate bodies, as follows:

[1] After sending this article to the editor, our attention was first directed to a note by Mr. W. Tistschenko, in the October Journal. Although in many respects our results are identical with his, it still seems to us desirable to publish them, since our method is not the same, and since related facts not hinted at in the note above mentioned have been observed in the course of our research. It is our purpose to complete the work already begun with methyl and the two propyl alcohols.

[2] This Journal, **18**, 621.

[3] J. Chem. Soc., 1881, **39**, 1; 1882, **41**, 5; 1886, **49**, 25.

(*a*) $3C_2H_5OH + Al_2I_6 = Al_2(C_2H_5O)_3I_3 + 3HI$;
(*b*) $Al_2(C_2H_5O)_3I_3 + 3C_2H_5OH = Al_2(C_2H_5O)_6 + 3HI$;
(*c*) $6HI + Al_2 = Al_2I_6 + 3H_2$.

The contents of their flask was then heated in an oil-bath to about 300°, and held at this temperature until the excess of alcohol had been driven off.

The residue in their flask was next distilled under diminished pressure[1] and a yellowish white distillate obtained which melted at 115° C.,[2] and boiled somewhere near the limits of the ordinary mercurial thermometer. This substance, to which they gave the name aluminum ethylate, was found to be quite free from iodine, and to contain considerable aluminum. It dissolved slightly in absolute alcohol, and from alcoholic solution water precipitated aluminum hydroxide. Heat at atmospheric pressure decomposed it into aluminum oxide, alcohol, ethylene, and ether.

Even though distilled *in vacuo*, they found considerable decomposition taking place, and on analysis it was usually found that there was from 1 to 2 per cent. of aluminum present in excess of that which the ethylate would require.

Wislicenus and Kaufmann observed in their recent work on amalgamated aluminum[3] that when they used it for the reduction of nitrobenzene, amyl nitrite, and similar substances in absolute alcoholic solution, a violent reaction took place, and a semi-solid mass was formed which they supposed to be a mixture of aluminum hydroxide and aluminum ethylate, but from which it was impossible to isolate any of the latter substance by distillation *in vacuo* according to the method of Gladstone and Tribe. The aluminum, however, had apparently gone into combination with the alcohol, and upon addition of water to the mixture separated out as the hydroxide.

In work with amalgamated aluminum prepared after the method of Wislicenus and Kaufmann[4] for the purpose of reduction in neutral solutions, a reaction was observed which led to an investigation—one part of which we have just completed, but which we began before the second article of Wislicenus and Kaufmann came to our notice.

[1] J. Chem. Soc., 1876, **29**, 161. [2] Given by them in a later article as 130° C.
[3] Ber. d. chem. Ges., **28**, 1985. [4] Ber. d. chem. Ges., **28**, 1323.

Aluminum in the form of fine chips cut from the block by means of a milling machine was amalgamated according to their method of first etching it with caustic soda, washing with water to remove the alkali, and then treating with an aqueous solution of mercuric chloride until strong evolution of hydrogen began. According to the authors, the amalgam thus prepared could be kept ready for use under dehydrated petroleum ether after first washing with alcohol and ether to remove any remaining traces of water. We experienced considerable difficulty, however, in obtaining an amalgam which had not become somewhat deteriorated by the necessary exposure to the air in preparation. To overcome this difficulty it occurred to us that we might bring about the amalgamation without contact with the air, or of moisture of any kind, by using a solution of mercuric chloride in absolute alcohol. We should then be able to use the amalgam in this solution for neutral reductions by simply adding water for the amalgam to act upon.

A solution of mercuric chloride in ordinary absolute alcohol was first used, and an evolution of gas observed. Thinking this to be due to the presence of moisture, we distilled some absolute alcohol which had been subjected to the action of our amalgam for some time, and found even with this alcohol, which could scarcely contain any water, that we had a reaction which was as violent, if not more so, than the action of the amalgam on water itself. It was further observed that the action continued with constant evolution of gas, and considerable rise in temperature, until the contents of our flask became, first gelatinous, and finally solid.

During the reaction the mercuric chloride became reduced, and considerable metallic mercury was to be seen at the bottom of the flask. On treating with water the substance gave a copious precipitate—apparently aluminum hydroxide—and the odor of alcohol was quite evident. This, together with the reaction itself, suggested that possibly we had aluminum ethylate formed. The reaction seemed to be rather remarkable, however, because, according to Wislicenus and Kaufmann, aluminum amalgam does not decompose absolute alco-

hol,[1] and also because, according to Gladstone and Tribe, aluminum chloride, which might be formed, gives no reaction even when boiled with absolute alcohol and aluminum.[2] We interpreted it, however, to be due to the joint influence of the aluminum-mercury couple and to the aluminum chloride formed in the reduction of the mercuric chloride.

Knowing from the work of Gladstone and Tribe that aluminum alcoholates, in contrast with all other known alcoholates, can be distilled under diminished pressure, we then attempted to distil the product obtained in our first reaction. Distillation was begun under a pressure of 20 mm. On applying heat the substance melted, white fumes being given off, and upon heating to the boiling-point, a transparent liquid passed over. This became grayish white as it cooled in the receiver, and was found to contain aluminum and some mercury. It had the consistency of beeswax, and possessed a very peculiar, though not disagreeable odor. The residue in the retort was of a varnish-like appearance, insoluble in the ordinary solvents. It still contained unchanged aluminum.

The distillate, which we supposed to be aluminum ethylate, was found to decompose with extreme rapidity when in contact with the moisture in the air, and also when heated at the atmospheric pressure.

In order to avoid the use of mercury, which not only caused trouble on distillation due to "bumping," but also passed over and contaminated the distillate, we made experiments with other anhydrous chlorides in the hope of finding a method of overcoming this difficulty.

Platinic chloride dissolved in the same manner in absolute alcohol gave, with chipped aluminum, an evolution of gas, but the action was not as violent nor of as long duration as with mercuric chloride. The platinic chloride was broken up like the mercuric chloride, metallic platinum being deposited on the walls of the flask. Fuming stannic chloride was next tried, and a very violent reaction resulted, hydrogen being rapidly evolved, and spongy tin being deposited on the aluminum.

[1] Ber. d. chem. Ges., **28**, 1324. [2] J. Chem. Soc., 1876, **29**, 162.

An experiment was then carried out with stannic chloride. 5 grams of chipped aluminum, and 1 cc. of fuming stannic chloride in 50 cc. of absolute alcohol were used. The action began at once and was accompanied by a considerable rise in temperature. It continued at the temperature of the laboratory for three or four days, when the contents of the flask had become quite solid. This was then distilled as before, and all precautions were taken to obtain the substance in as pure condition as possible. Distillation was begun at a pressure of 23 mm. Gentle heat was applied until the contents of the distilling flask had reached almost the boiling-point, and continued for some time until all of the white fumes had passed over. A distilling flask was then placed in position as a receiver, and as much of the substance as would distil without decomposition was allowed to pass into it. This flask was then disconnected, provided with a thermometer, and the contents fractionated under diminished pressure with an apparatus resembling that used by Brühl for fractionation *in vacuo*, but modified slightly to enable us to heat the receiver quite hot in an air-bath.

The substance boiled evenly during the distillation, and the thermometer rose slowly from 235° C., as the first portion began to come over, to 245° C., when the distillation was complete. Our distillate, which we collected in three portions, was a clear transparent liquid which, on cooling, became white and opaque, owing to an apparent tendency to crystallize, but still of a gummy consistency. It melted at 135° C. and boiled constantly, within the above-mentioned range, at a pressure of 23 mm. It was only very slightly soluble in absolute alcohol, but more so in ether and benzene. Chloroform did not dissolve it. That obtained in this experiment possessed the same peculiar odor as had been noticed before. The middle portion was analyzed for aluminum. The average of six determinations by ignition, after treating with nitric acid, resulted in showing that it contained 18.13 per cent. of aluminum. As this was considerably in excess of the theoretical amount in aluminum ethylate (16.66 per cent.) it was decided that our distillate was either a mixture of aluminum ethylate and aluminum hydroxydiethylate—a sub-

stance which we think might easily result from a partial de composition due to presence of moisture in the alcohol—or that it contained an impurity from which, as yet, we had been unable to free it.

A test in our latest distillate showed the presence of chlorine, and we decided, therefore, that the excess of aluminum in our ethylate must be due to the presence of some aluminum chloride, which volatilized at a low heat, and condensed along with our substance in the receiver.

In a later experiment, where we used as high a quantity as 6 cc. of stannic chloride, in order to determine whether the amount of chloride had any influence on the rate of reaction, it was found, on heating to distil, that there was scarcely any substance present which would fuse, and that the white fumes, which had been only moderate in other cases, were now greatly increased, and condensed as a feathery mass in the receiver. This, on analysis, was found to be aluminum chloride.

	Calculated for $AlCl_3$.	Found.
Aluminum	20.22	20.13

A new portion was made up, and distilled several times in order to obtain it free, if possible, from aluminum chloride, but without success.

Determinations were then made of the amount of chlorine and aluminum contained in the same sample, and it was found that, deducting the amount of aluminum which was present as aluminum chloride, there remained an average of 17.71 per cent. of aluminum to be accounted for as the ethylate, and, although this percentage is large, we consider it entirely within the limits of error of analysis, on account of the hygroscopic character of the ethylate.

	Calculated for $Al(C_2H_5O)_3$.	Found. I.	Found. II.
Aluminum	....	18.05	17.76
Chlorine	....	6.15	6.09
Aluminum as ethylate	....	....	....
	16.66	17.86	17.57

These analyses show that it corresponds more closely to the ethylate than to any other substance likely to be formed.

Experiments were carried out in order to see whether the amount of stannic chloride used had any effect either upon the rate of reaction or upon the amount of ethylate formed.

Amounts of chloride varying from 1 to 6 cc. were used with the usual amounts of aluminum and alcohol. The results showed that, when large amounts of chloride were used, the contents of the flask became solid much more quickly, but that the mass consisted almost entirely of aluminum chloride which, on heating under diminished pressure, volatilized and condensed as before stated in the receiver. But little ethylate was formed.

The reaction is more successful when small amounts of stannic chloride are used, even though it takes place more slowly.

An effort was made to free the distillate from chlorine by distilling it in presence of lead oxide. This was not successful, however. There was decomposition on heating, and the distillate obtained was still contaminated with chloride.

As to the reactions involved in what we call our aluminum-stannic chloride reaction, we can only say, that we believe it to be due to the joint action of the couple and the aluminum chloride, neither of which alone seems to be capable of bringing it about. The couple prepared by using an alcoholic solution of stannic chloride, and washing to remove all traces of chloride, proved inactive, but, when freshly prepared aluminum chloride, made by the action of hydrochloric acid gas on aluminum, was added, the reaction began at once. Without the tin, however, the chloride had no effect in the presence of aluminum. The increased rapidity of action when increased amounts of stannic chloride are added, may also be attributed to the influence of the greater amounts of aluminum chloride formed in the initial reaction.

The ethylate we have obtained by this reaction shows properties similar to those found by Gladstone and Tribe. In color, however, ours was of a pure white, while theirs is described as yellowish-white. This color, we think, from their reaction might very easily be due to the presence of a slight trace of iodine.

In further work with the alcoholates prepared by means of our aluminum-stannic chloride reaction we hope to throw more light on some of those points which are as yet not quite clear.

ORGANIC CHEMICAL LABORATORY,
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October 12, 1896.

ON THE CONDITIONS AFFECTING THE VOLUMETRIC DETERMINATION OF STARCH BY MEANS OF A SOLUTION OF IODINE.

BY FANNIE T. LITTLETON.

The investigation of which this paper is an account was undertaken at the University of Virginia, under the direction of Dr. J. W. Mallet, for the purpose of ascertaining if a satisfactory process for the volumetric determination of small quantities of starch can be based on the colorimetric use of the so-called iodide of starch.

After the investigation had been completed, an article of 16 pages, summarizing the results of various previous workers, on the various methods of determining starch, appeared in the *Zeitschrift für analytische Chemie* of Fresenius (35ter Jahrg, S. 607). Among the methods mentioned are several based on the use of iodine. The results of many efforts to estimate the amount of iodine held in combination by 1 gram of starch were found to vary so greatly as to warrant the conclusion that a firm union between the two does not exist, but the amount of starch iodide formed is dependent upon the concentration of the solution. A colorimetric determination by means of the iodine reaction is noted, the work being done by M. Dermstedt and F. Voigtländer. The authors recommend the use, as a standard, of a pure starch of the same kind as the one to be estimated, for instance with wheat flour, wheat starch. For accuracy, the average of a great number of estimations is recommended. The authors set forth as the advantages of this method the rapidity and ease with which it may be carried out, and the fact that the result gives starch alone, unmixed with other carbohydrates.

At the beginning of my work a solution of 0.1 gram to the

liter, wheat starch being used as the working material, was found to be a convenient strength. Ten cc. of this solution, to which 0.75 cc. of a standard solution of iodine (1 gram to the liter) was added, when diluted to 50 cc., gave a blue color of depth suitable for accurate recognition of differences in intensity.

The standard solution of iodine was made by dissolving iodine in a solution of potassium iodide in the proportion of 1 atom of the former to 1 molecule of the latter—iodine 126.5 to potassium iodide 165.5.

In all the following experiments the starch used was dried to a constant weight.

Using the wheat starch solution above mentioned and the standard iodine solution, the influence of temperature was first examined. It was found that a rise of 5°, or less than this produced no clearly perceptible effect; above this the color of the solution became perceptibly fainter, and almost disappeared when 15° additional had been reached.

The starch dissolving in water alone only after long continued boiling, the effect of the addition of alkali was tried. It was found that as little as 0.002 gram of potassium hydroxide was sufficient to cause 1 gram of starch to dissolve easily, larger quantities having the same result and producing no effect upon the color of the starch iodide solution if the solution was carefully neutralized with acid before the iodine was added.

Solutions of various kinds of starch were then compared. Taking as 100 an exceptionally pure specimen of arrowroot starch (which was used as a standard in all experiments following), by comparing the heights of columns of corresponding color taken from solutions of equal amounts of starch, the strengths, varying inversely as the heights of the columns, were as follows:

Arrowroot	100
Potato	97.06
Wheat	94.81
Tapioca	90.41
Rice	83.83

These results agree with what we should expect, consider-

ing the known size of the starch granules. The determination of the amount of true starch by the starch iodide formed, represents only the granulose, since the cellulose or outer covering of the granules gives, in its normal state, no reaction with iodine. Rice starch, having smaller granules and hence a relatively larger surface and probably a proportionally large amount of cellulose, we should not expect to show as great a percentage of true starch as the arrowroot with its larger granules.

Taking a standard starch solution of 0.0001 gram to the cc. and a standard iodine solution of 0.00008 gram to the cc., the relative amounts of starch and iodine necessary to produce the maximum color were found in various cases as follows:

Starch.		Iodine.
0.007 gram	required	—0.00448 gram.
0.006 "	"	—0.00384 "
0.005 "	"	—0.00320 "
0.004 "	"	—0.00256 "
0.002 "	"	—0.00128 "
0.001 "	"	—0.00064 "

From which it appears that the varying amounts of iodine used are proportional to the amounts of starch.

Taking the same amount of starch, from a solution, 1 cc. of which contains 0.0002 gram, with iodine solutions of different strengths, the maximum color was obtained with the following results:

Starch.		Iodine.
0.002 gram	with iodine solution of 0.05 gram to liter required	0.00175 gram.
0.002 "	" " " " 0.08 " " " "	0.00128 "
0.002 "	" " " " 0.1 " " " "	0.00128 "
0.002 "	" " " " 0.2 " " " "	0.00160 "
0.002 "	" " " " 0.4 " " " "	0.00120 "

This shows the dissociating effect of the additional water contained in the weaker iodine solutions, also that the conclusion from the first table is only true when a solution of iodine of a single strength is used.

To trace, if possible, some law for the dissociating effect of water, the set of experiments below were made. I took 0.005 gram starch in 20 cc. of water, found the maximum color produced by the addition of 0.002 gram iodine (from a solution 0.2 gram to the liter) and diluted the mixture to 50 cc. I

then took a mixture consisting of 95 per cent. of the above amount of starch (the solution being of the same strength) and a proportional amount of iodine from the solution used in the first case. Diluting the mixture to 50 cc. and comparing strengths by the heights of columns of the same depth of color, the apparent amount of starch present was 88.16 per cent. of the standard. In the same way I found the results expressed in the table below, taking in every case the average of four experiments.

Actual amounts of starch. Per cent.	Apparent amounts of starch. Per cent.
100	100.00
95	88.16
90	84.98
85	74.50
80	71.40
75	68.85
70	62.23
65	55.88
60	50.95
55	46.99
50	39.84
45	36.86
40	24.33
35	21.87
30	14.27

Amounts below 30 per cent., when diluted to the standard volume, gave practically no color.

The above table was taken with solutions whose temperatures varied from 33°.6 to 32°.6.

From this it appears that it will be necessary in using the method to compare substances whose percentages of starches do not differ widely.

After the maximum color had been obtained, an additional amount of starch was found to deepen the color until a second maximum was reached, when more starch had no effect. The same result was observed when less than the amount of iodine required for a maximum color was used. This would suggest the inference that the iodine dissociated by water will enter into combination with additional starch. The

starch solutions used were more concentrated than those used above, 1 cc. being equivalent to 0.8 milligram.

Finding roughly by use of the iodine reaction that oatmeal contained 38 per cent. of starch, equal volumes of the oatmeal and standard starch solutions were prepared to contain, according to this result, equal amounts of starch. By means of this comparison, however, the oatmeal showed a smaller percentage than that calculated. Concluding this might be due to the presence of albuminoid matter an investigation was made to determine the effect of such matter.

One gram of pure arrowroot starch was dissolved in a liter of water, and, at the same time, another solution in an equal volume of water of 1 gram of a mixture consisting of 50 per cent starch, 10 per cent. cellulose (paper) and 40 per cent. albuminoid matter (white of egg). These solutions were compared, but the amounts of starch, instead of standing as 2 to 1 appeared as 8 to 1. The mixture behaved as if it had 0.25 the amount of starch which had been used in making it. The color also was rather violet than blue.

The percentages of starch in dried specimens of bread, potato, and fine white wheat flour (taking 1 gram to the liter) were estimated with the following results:

	Per cent.
Bread	41.72
Potato	38.64
Flour	45.60

Of substances containing little starch peanuts and chocolate beans were taken, one trial being made after the fat had been removed by repeated washing with ether, the other before its removal. In both cases the solutions gave no perceptible color with iodine.

In Thorpe's Dictionary of Applied Chemistry, Vol. 3, p. 565, it is stated that when iodide of starch does not contain an excess of iodine, alcohol, ether, carbon bisulphide, or benzene fails to extract any iodine from it. To verify this I took 20 mgs. of starch, added less than one-fifth the iodine necessary to produce the maximum color, diluted to 250 cc., and added chloroform. After shaking vigorously for a few minutes the blue color disappeared from the solution and the chloroform

globules were decidedly violet. This seems to show that the iodide, *in the wet state at least*, is acted upon by chloroform. A like result was obtained with carbon bisulphide.

As a general conclusion it appears that, on account of the dissociating effect of water on starch iodide, the method is available only with substances containing a large amount of starch, and is best used when the substances compared contain starch in proportions not widely differing. In fact, the solutions to be colorimetrically compared must be in all respects under conditions very nearly identical. This greatly narrows the limits within which this method is available in the examination of food materials, though occasionally cases may present themselves in which it will have a certain value.

The results of all the experiments made seem to confirm the belief that the so-called iodide of starch, if a chemical compound, is one very easily dissociated, by rise of temperature, by increase of the amount of solvent water, and by the introduction of another liquid, such as chloroform, etc., of superior solvent power.

Contribution from the Chemical Laboratory of Dartmouth College.

SILVER HYDRIDE.

By Edwin J. Bartlett and William F. Rice.

Hydrogen forms binary compounds with all the non-metallic elements. The most generally known hydride is water; the hydrides of sulphur and the halogens are acids; other well known ones are ammonia, NH_3, phosphine, PH_3, methane, CH_4, hydrogen peroxide, H_2O_2, arsine, AsH_3, and stibine, SbH_3.

Many cases occur in electrolysis, where the metal used as the negative electrode absorbs hydrogen. Examples of this are palladium, platinum, iron, nickel, gold, silver and aluminium, but the action here is without doubt almost entirely physical.

In a different manner, however, hydrides have been formed of two of the metals above mentioned. Palladium has been found to be able to absorb hydrogen to a most remarkable degree; namely, to almost one thousand times its own volume.

During this process of absorption it was found, first by Graham,[1] in 1866, and verified later by others,[2] that a definite compound of palladium was formed at about 100° C., having the composition indicated by the formula Pd_4H, and that this compound continued to occlude or absorb hydrogen, with or without the further addition of heat. This hydride could not be obtained by precipitation with the chloride or sulphate and hypophosphorous acid,[3] but the metallic sponge thus formed had the property similar to the cupric hydride discovered by Merrill,[4] of indefinitely decomposing the acid with the evolution of hydrogen. In 1862 Wanklyn and Carius[5] prepared a hydride of iron from ferrous iodide and zinc ethyl, but did not determine the formula.

Hydrides of potassium[6] and sodium are known. Both are made[7] by heating the metals in an atmosphere of hydrogen. Potassium hydride, K_2H, is formed at 200° C., sodium hydride, Na_2H, requires a higher temperature.

Recently lithium hydride,[8] LiH, has been prepared and analyzed. It decomposes water with the evolution of hydrogen.

Two hydrides of copper are known. Cuprous hydride, CuH or Cu_2H_2, was discovered in 1844 by Würtz.[9] The existence of this hydride has been denied by Berthelot,[10] who claimed that the so-called hydride was a mixture of water, oxygen and phosphorus, or perhaps a complex phosphated hydroxide of copper, formed by the mixture of several compounds. Würtz subsequently maintained his side and pointed out the errors in Berthelot's work.

Cupric hydride was discovered last year by Mr. W. H. Merrill in the Chemical Laboratory of this College. Würtz had obtained his hydride by precipitating copper sulphate with barium hypophosphite, and it is reasonable to suppose

[1] Phil. Mag. (4), **32**, 516; Proc. Roy. Soc., **15**, 502; **16**, 422.

[2] Troost and Hautefeuille: Compt. Rend., **78**, 686, 968; Dewar: Phil. Mag., **47**, 334; Favre: Compt. Rend., **71**, 214; **77**, 649; **78**, 1257; **68**, 1306, 1520; Thorne: Ztschr. phys. Chem., **3**, 69; **17**, 1.

[3] Engel: Compt. Rend., **110**, 786. [4] This JOURNAL, **17**, 185.

[5] Ann. Chem. Phys., **130**, 69. [6] Gmelin's Handbook, (Watt's Trans.), **3**, 17.

[7] Troost and Hautefeuille: Compt. Rend., **78**, 807.

[8] Guntz, Compt. Rend., **122**, 244.

[9] Compt. Rend., **18**, 702; Ann. Chim. (3), **11**, 250.

[10] Compt. Rend., **89**, 1005.

that at some stage in the process he must have had cupric hydride. Mr. Merrill in his work used hypophosphorous acid itself and took great care to prevent the cupric from changing to cuprous hydride and then to the metallic sponge.

His analyses showed the formula to be CuH_2. As before mentioned, this substance has the power of indefinitely oxidizing hypophosphorous to phosphorous acid, the action having no effect on the hydride and taking place at the ordinary temperature. He describes the hydride as a reddish-brown sponge-like mass when freshly prepared, changing to a chocolate-colored powder on being freed from acid and boiled in water.

In carrying on the work begun by Mr. Merrill last year, particular attention was given to finding and analyzing the hydride of silver. We also obtained a hydride of mercury, but have made no quantitative determinations.

The silver hydride was prepared by precipitating a dilute solution of silver nitrate with dilute hypophosphorous acid in excess. The mixture becomes first wine-colored, changing almost immediately to black, often showing a silvery lustre on the sides of the containing vessel. The rapidity of the color change is lessened as the original solutions are made more dilute. At this stage it passes through filter-paper, staining it black. After standing two or three minutes a black product begins to settle in small spongy flakes. In about five minutes the supernatant liquid is decanted off. The yield of precipitate is not very large, but longer standing soon changes the hydride to silver. The decanted liquid on standing or boiling deposits all the remaining silver in a sponge.

The precipitate is immediately washed with cold water until free from acid, thoroughly dried at about 60° C. to constant weight and ignited in a porcelain crucible to constant weight. The product is then bright metallic silver.

Considerable difficulty is found in getting good samples of the hydride, the precipitate when dry appearing lighter in color the greater the proportion of silver present. This was proved to be the case when the computations came to be made.

The formula AgH requires 99.074 per cent. of silver, the atomic weight of Ag being 107.9 and that of H 1.008.

Fourteen determinations resulted as follows :

Substance taken. Gram.	Silver obtained. Gram.	Per cent. silver.
0.2613	0.2597	99.38
0.0268	0.0266	99.23
0.06945	0.0689	99.21
0.05975	0.05925	99.16
0.08525	0.08443	99.04
0.03865	0.03841	99.38
0.14359	0.14277	99.43
0.1647	0.16322	99.10
0.09563	0.09500	99.34
0.0809	0.08041	99.39
0.16339	0.16240	99.39
0.16353	0.16213	99.14
0.20940	0.20815	99.40
0.16552	0.16465	99.47

Average, 99.289 per cent. ; difference from computed value, 0.22 per cent.

To test the accuracy of the above results several experiments were performed by treating in the same manner some of the silver sponge obtained in the course of preparing the hydride. Amounts varying from 0.18783 gram to 3.75008 grams of the sponge were taken and in all cases the silver found was between 99.835 and 99.936 per cent.

Silver hydride is not decomposed by water, nor does it evolve hydrogen in the presence of hypophosphorous acid.

DARTMOUTH COLLEGE,
JUNE, 1896.

Contribution from the Laboratories of the Massachusetts Institute of Technology.

XV.—ON THE VOLATILITY OF FERRIC CHLORIDE.

BY HENRY P. TALBOT.

The analytical examination of iron-bearing bodies involves the frequent heating of ferric chloride solutions, as well as the occasional continued heating of the residues which such solutions leave after evaporation, and the accuracy of such analyses is dependent upon the permanency of the iron under the prevailing conditions. The writer has frequently noted an apparent deposit of ferric chloride upon the outer edge of watch-glasses used as covers for solutions during evaporation, which suggested a possible

loss of iron. An examination of the literature revealed the existence of conflicting statements bearing upon the volatility of ferric chloride, and an absence of data relating to its behavior under such conditions as prevail when a residue of chlorides and silicic acid is heated to accomplish the dehydration of the latter, as in the analysis of silicates.

Fresenius,[1] in 1867, published a series of experiments from the results of which the conclusion is drawn that no loss of ferric chloride occurs during the processes of evaporation, either when the solutions are rapidly boiled, or indeed, when the residues are subjected to prolonged heating at the temperature of the water-bath. The procedure adopted for the determination of the iron was that of titration with stannous chloride, and the determination of the excess of the latter by titration with iodine. No data are presented bearing upon a possible loss of the chloride at temperatures as high as 125° or 130° C., at which silicic acid is commonly dehydrated.

But, on the other side of the question stands the statement of Vogel,[2] made in 1869, that traces of ferric chloride are volatilized from aqueous solutions, even at temperatures below 100° C., and that such volatilization occurs at temperatures as low as 30° C., in the presence of ether. He calls attention to the obvious possibility of loss of iron during the course of analysis, as a result of this volatility.

More recently, Browne[3] has made a statement to the effect that a loss of ferric chloride is to be feared "if its solution be too strongly heated," which he seems to consider a possible source of error in the analysis of iron ores, against which the chemist is to be cautioned. It seemed desirable, in the light of these varying statements, that the subject should be again investigated.

The experiments which Vogel described were repeated with substantially the results which he published, with the one exception, that but little difference was observable qualitatively between a very concentrated aqueous solution of ferric chloride, and an ethereal solution. A paper (frequently moistened throughout the day with potassium sulphocyanate solu-

[1] Ztschr. anal. Chem., 6, 92. [2] N. Rep. Pharm., 18, 157.
[3] J. Anal. Appl. Chem., 1891, 342.

tion), which covered a beaker containing the ether solution, showed some evidence of iron on standing over night. To determine qualitatively whether the ether vapor would promote the volatilization of the ferric chloride to a marked degree, an ethereal solution was subjected to distillation on the water-bath, but the distillate, after shaking with water, yielded only the faintest trace of iron, and a similar result was recorded when ether vapor was passed into a concentrated boiling solution of the chloride. No quantitative determinations were attempted, since in the light of other experiments, these seemed superfluous.

The ferric chloride solutions employed in the following experiments were prepared from the sublimed chloride, and were themselves very nearly neutral. They were measured from a burette into a porcelain dish, or small casserole, and evaporated as described in the various paragraphs below. The residues were moistened with 15 cc. of hydrochloric acid (1.12 sp. gr.), and brought into solution by warming. The reduction was effected while hot, by the cautious addition of stannous chloride solution,[1] avoiding the addition of more than a few drops in excess, after which this excess of tin was oxidized by the addition of 10 cc. of a mercuric chloride solution (50 grams to the liter). After an interval of three minutes, to allow complete precipitation of the mercurous chloride, the ferrous iron was titrated with a standard solution of potassium bichromate, the end-point chosen being that at which no blue could be detected after a contact of the iron and ferricyanide solutions lasting thirty seconds. The end-point may be determined with certainty and accuracy, by placing upon a white surface, such as a glazed porcelain tile, several small drops of the indicator solution (which has been freshly prepared, and so far diluted that it retains but little color[2]), mixing a drop of the iron solution with one of these, and at the end of the thirty seconds, mixing a second drop of the solution, with the drop of the indicator next the first test. If ferrous iron is present, causing precipitation during the interval of thirty seconds, the first portion will be

[1] Made by allowing hydrochloric acid to act upon metallic tin until action ceases, and diluting with an equal volume of water.

[2] The solution of a crystal of potassium ferricyanide of the size of a pin head in 25 cc. of water is ample.

seen to be darker than the fresh mixture. The end-point has been reached only when no difference in shade can be detected. Carried out in this way, the bichromate process for the determination of iron may be considered to be thoroughly reliable. The number of tests required to fix the end-point are small, particularly when the character of the material under examination is approximately known; and when the great advantage which the bichromate process offers in the use of hydrochloric acid solutions is considered, the time consumed by this process compares favorably with that necessary for the more popular permanganate process.

The potassium bichromate solutions used were approximately, decinormal, and fiftieth normal. They were standardized against iron wire, and the iron contents of the ferric chloride solutions was determined by titration with these solutions, according to the procedure outlined above. The reagents were carefully tested for iron.

Behavior of Ferric Chloride Solutions when Heated.

The first ferric chloride solution used contained, in 25 cc., 0.2201 gram iron (Fe); the mean of four determinations, 0.2205, 0.2202, 0.2199, 0.2199.

Of this solution 25 cc. evaporated to dryness on the water-bath, yielded 0.2201, 0.2201, and 0.2205 gram Fe; mean, 0.2202 gram Fe.

Of the same solution 25 cc., acidified with 15 cc. of hydrochloric acid (1.12 sp. gr.), and evaporated on the water-bath, yielded 0.2200, 0.2200, 0.2203 gram Fe; mean, 0.2201 gram Fe.

Of the same solution 25 cc., with 15 cc. of hydrochloric acid, evaporated to dryness on the water-bath, and the residue subsequently heated for two hours (the time usually assigned as necessary for the dehydration of silicic acid) at 130° C., yielded 0.2205, 0.2203, 0.2199 gram Fe; mean, 0.2202 gram Fe.

The titrations above were made with decinormal potassium bichromate solution only. In the experiments cited below, the decinormal solution was added until the end-point was nearly reached, and the titration then completed with fiftieth normal

solution in the hope that small differences in the amounts of iron present might be more readily detected. It is perhaps doubtful if the results may properly be considered to be more accurate than with the decinormal solution alone. They are presented as cumulative evidence.

A second ferric chloride solution was found to contain, in 25 cc., 0.1741 gram Fe, as a mean of six determinations.

Of this solution 25 cc. evaporated on the water-bath, and the residue subsequently heated for two hours at 130° C., yielded 0.1739, 0.1738, 0.1742, 0.1739, 0.1739, 0.1737 gram Fe; mean, 0.1739 gram Fe.

Of the same solution, 25 cc. evaporated to dryness on a hot plate, and the residue heated as above, yielded 0.1742, 0.1737, 0.1741, 0.1742 gram Fe; mean, 0.1740 gram Fe.

In order to test an extreme case, three portions, of 25 cc. each, of the ferric chloride solution were evaporated to dryness on the hot plate, and the residues subsequently heated over the free flame for three minutes in each of two instances, and for half an hour in the third. The amounts of iron found in the residues were 0.1735, 0.1738, and 0.1736. While these figures indicate a slight loss of iron, the amount is less than 0.4 per cent. of the iron present, even under these extreme conditions.

The foregoing results confirm the statements made by Fresenius, that ferric chloride is not volatilized by boiling its solutions, and show, in addition, that no loss of iron ensues on heating the residues from these solutions in the hot closet, at 130° C. Browne states, in the paper already cited, that a filter paper moistened with potassium sulphocyanate solution, and held above a boiling ferric chloride solution will give ready proof of the presence of the latter in the escaping vapors. Repeated experiments bearing upon this point showed that the evidences of the presence of iron upon the filter paper, when they were to be found at all, were of such a character as to indicate that minute drops were projected upward by the boiling liquid, rather than that a volatilization of the iron, in a strict sense, had occurred.

Other experiments were made in which several portions of a very concentrated ferric chloride solution, both with and

without the addition of acid, were distilled in a flask provided with an exit tube so bent as to make mechanical transfer of iron from the flask to the condenser impossible, and the distillation cautiously continued to dryness. In no instance could any iron be detected in the distillate, until the ferric chloride had separated from solution, and had been volatilized in the moist, acid atmosphere by the overheating of the sides of the flask. The conditions within the distillation flask, as a result of the partial condensation and return of the aqueous vapor charged with hydrochloric acid, differ from those which prevail during evaporation in open dishes, and are probably more favorable to the volatilization of the iron salt at the moment of its separation from solution. As is well known, ferric chloride solutions lose acid during evaporation in open vessels, with the formation of basic salts, which may reasonably prevent the possible volatilization of the unchanged chloride, until it, in turn, has become basic.

In order to study a little more closely the behavior of the chloride during evaporation, and when heated to a definite temperature, 25 cc. of a solution (containing 0.2210 gram Fe), were placed in a small flask immersed in an oil-bath, and a slow current of dry air passed over the solution at a temperature of about 100° C., until it had evaporated to dryness, after which the temperature was raised to 195° C. for an hour or more. The air current, after leaving the flask, passed through water, to retain any ferric chloride which it might carry with it. Only a slight coloration could be obtained with potassium sulphocyanate in this water, and the residue in the flask yielded 0.2203 gram Fe. A second portion heated to 250° C. yielded 0.2204 gram Fe. Since the boiling-point of ferric chloride is stated by Friedel and Crafts[1] to be 280°-285° C., it appears that very little, if any, of the iron remains as unaltered ferric chloride, otherwise the trifling loss of iron at a temperature so near the boiling-point of the chloride could hardly be explained.

Behavior of Ferric Chloride in the Presence of Ammonium Chloride.

It seemed desirable to extend the experiments in such a

[1] Compt. rend., 107, 301.

way as to include solutions which, beside the ferric chloride, should also contain ammonium chloride.

To three portions of 25 cc. each, of a ferric chloride solution (containing 0.1739 gram Fe), was added 1 gram of ammonium chloride, the solution evaporated to dryness on the plate, and the residue heated for two hours at 130° C. The amounts of iron found in the residues were 0.1742, 0.1742, 0.1739 gram Fe (mean, 0.1741 gram Fe), indicating that the presence of the ammonium salt does not occasion a loss of iron within the limits named.

As would be expected, stronger heating in the presence of the ammonium salt led to volatilization of the iron. A portion of the solution, prepared as above, when evaporated to dryness on a hot plate and allowed to remain on the plate until the ammonium chloride had been slowly, but completely expelled, still yielded 0.1718 gram Fe, while two other portions (each containing 0.1747 gram Fe), which were heated over a free flame until ammonium chloride fumes first appeared, yielded 0.1745 and 0.1746 gram Fe. Still other portions of the same solution which were strongly heated over a free flame until the ammonium salt was entirely expelled, yielded only 0.1542 and 0.1643 gram Fe.

Behavior of Ferric Chloride in the Presence of Nascent Chlorine.

To determine the behavior of ferric chloride in the presence of nascent chlorine, 25 cc. of a solution (containing 0.1739 gram Fe), were mixed with 5 cc. of a mixture of three parts of hydrochloric acid (sp. gr. 1.2) and two parts of nitric acid (sp. gr. 1.42), and the mixture was evaporated to dryness on the plate, after which the residues were heated for two hours at 130° C. The iron found in each of three such portions amounted to 0.1730, 0.1730, 0.1729 gram. A second series of three portions (each containing 0.1747 gram Fe), was evaporated on the water-bath, and heated as above. These yielded 0.1742, 0.1737, 0.1738 gram Fe. The data furnished by these experiments indicate a tendency toward a loss of iron in the presence of the nascent chlorine, or the nitric acid. The maximum deficiency represents only 0.6 per cent. of the total iron.

In summarizing, it may be said that the results show that no loss of iron, in the form of ferric chloride, is to be feared under the conditions which prevail in ordinary analytical procedures, unless residues containing also ammonium chloride are overheated, or, in the presence of aqua regia, where a small, but appreciable loss of iron appears to be possible.

In conclusion, acknowledgment is gladly made of the writer's indebtedness to Messrs. R. F. Hosford and G. M. Goodspeed for painstaking analytical work, the results of which are embodied in the foregoing discussion.

CONCERNING PROPERTIES BELONGING TO THE ALCOHOL-SOLUBLE PROTEID OF WHEAT AND OF CERTAIN OTHER CEREAL GRAINS.

By G. L. Teller.

In attempting to work out a method for the ready quantitative separation of the proteids in wheat[1] based upon the properties of those bodies as described by Osborne and Voorhees,[2] and especially in attempting to separate the gluten and the non-gluten nitrogen compounds by thoroughly extracting a small quantity of the meal with dilute salt solutions, it was found that certain discrepancies occurred which made it apparent that considerable quantities of the same nitrogen compound or compounds were soluble both in dilute salt solutions and in 75 per cent. alcohol. It had also been ascertained by an extensive series of investigations that a considerably larger quantity of nitrogen compounds was extracted by a 1 per cent. than by a 10 per cent. solution of common salt (NaCl), and that for salt solutions between these strengths there was a gradual decrease of the amount of nitrogen compounds extracted as the salt solution contained more salt. Furthermore, the decrease did not stop with 10 per cent. salt solution, but was still seen when 15 per cent. and 20 per cent. solutions were used. Thus a sample of low grade flour gave the following results: One per cent. salt solution extract con-

[1] Full details of this work are given in Part II. of Bulletin No. 42 of the Arkansas Agricultural Experiment Station, which publication is now in press.

[2] This Journal, 15, 392–471.

tained 0.66 per cent. of nitrogen; 10 per cent. salt solution extract contained 0.48 per cent. of nitrogen; and 20 per cent. salt solution extract contained 0.20 per cent. of nitrogen to each gram of material extracted.

With the hope of finding the cause of this feature of the question a considerable quantity of perfectly clear 1 per cent. salt extract of wheat meal was obtained. To this a sufficient quantity of dry salt was added to make a 10 per cent. solution. A considerable precipitate was produced and this was found to be largely soluble in 75 per cent. alcohol, in a clear solution of which proteids were readily detected.

If the proteids, or a portion of them, which are soluble in salt solution are insoluble in alcohol they should be precipitated by the addition of alcohol to the salt solution. When 50 cc. of the clear, filtered, 1 per cent. salt extract of wheat were mixed with sufficient strong alcohol to make the resulting mixture contain about 75 per cent., a considerable white, flocculent precipitate was produced. This soon settled, leaving a clear liquid. The liquid filtered rapidly, giving a perfectly clear filtrate. The rapidity of flocculation of the precipitate increased somewhat on heating. The concentrated filtrate gave a strong biuret reaction. In like manner a marked biuret reaction for proteids was obtained by concentrating 100 cc. of alcohol filtrate when the added alcohol was such as to make 90 per cent. of alcohol in the mixture.

In following out this line of investigation a solution was made by mixing 100 grams of wheat meal with 500 cc. of 1 per cent. salt solution, shaking at intervals for one hour and filtering at the end of three hours. The proteids insoluble in 75 per cent. alcohol were precipitated from 40 cc. of this perfectly clear filtrate by the addition of such alcohol as was necessary to make a mixture of the desired strength. An aliquot portion of the resulting clear alcoholic filtrate, corresponding to 20 cc. of the original salt solution, was evaporated to dryness in a Kjeldahl flask, and a determination made of the amount of nitrogen it contained. Similar nitrogen determinations were made when a 10 per cent., and later a 15 per cent. salt solution was used for extracting like quantities of the same wheat. In this manner is found the number of milli-

grams of nitrogen in the nitrogen compounds soluble in alcohol from 20 cc. of the salt solutions of the various strengths. Determinations of the total nitrogen contents of each of these salt solutions were also made and computed to milligrams in each 20 cc. of solution. The results of both of these series of determinations are shown below:

	Total nitrogen. Milligrams.	Alcohol-soluble nitrogen. Milligrams
1 per cent. salt solution	19.48	9.7
10 " " " "	18.6	8.8
15 " " " "	16.2	7.6

It was found later that a part of this alcohol-soluble nitrogen is from amides, but the amount of amides in the wheat was by no means sufficient to account for the whole of the nitrogen thus obtained, and furthermore, abundant indications of proteids were found in each case by suitably concentrating the alcoholic filtrate and applying the biuret test.

A further comparison of the extracts obtained by 1 per cent. and by 10 per cent. salt solutions was made as follows: Salt extracts were made in 200 cc. measuring flasks, as hereafter described, using 4 grams of material, so that 50 cc. of the extract would correspond to 1 gram of the sample. This quantity of extract was mixed with 250 cc. of strong alcohol and allowed to stand over night. Nitrogen was then determined in both the filtrates and the precipitates with the following results:

Precipitated by alcohol.	Nitrogen. Per cent.
1 per cent. salt solution	0.21
10 " " " "	0.23
Soluble in alcohol.	
1 per cent. salt solution	0.42
10 " " " "	0.27

A similar trial on a sample of "ship stuff" gave results as follows:

Precipitated by alcohol.	Nitrogen. Per cent.
1 per cent. salt solution	0.31
10 " " " "	0.31

It seems clear that the difference in amounts of nitrogen compounds removed from wheat by 1 per cent. and by 10 per

cent. salt solutions is due to such as are soluble in 75 per cent. alcohol. Filtering hot did not materially affect the results.

A strong alcoholic solution of wheat proteids was made by mixing the meal with cold 75 per cent. alcohol. On pouring this clear extract into 1 per cent. salt solution a precipitate was produced which, when filtered off, gave a perfectly clear filtrate. Proteids in considerable quantity were detected in this filtrate by various reactions. Furthermore, the liquid was found to give the reactions characteristic of proteoses: Not coagulated by heat; a precipitate with nitric acid which disappeared on warming and reappeared on cooling; a like reaction with potassium ferrocyanide and acetic acid; precipitation by 20 per cent. sodium chloride and acetic acid. Authorities[1] also state that proteoses are precipitated by alcohol. Either we have here a proteose which is soluble in alcohol, or it is the result of the decomposition of a proteid which is soluble in alcohol, brought about by mixing the liquid with the 1 per cent. salt solution. If it be the latter, what is the explanation of the alcohol-soluble portion of the salt extract? When the alcohol solution of this salt-soluble proteid is concentrated it exhibits the properties of proteoses mentioned. It also, when concentrated somewhat, exhibits the character of gliadin solutions in alcohol, in that it is precipitated either by the addition of water or of strong alcohol.

A sample of fresh gluten was treated with hot 75 per cent. alcohol and 10 cc. of a resulting concentrated extract were poured into 90 cc. of 1 per cent. salt solution. A precipitate formed which, on the following morning, was filtered off and, by sprinkling a little pure, fine animal charcoal on the wet filter, a perfectly clear filtrate was obtained. This filtrate contained a proteid exhibiting the same proteose reactions mentioned above.

Some months previous a sample of gliadin had been prepared, at least nearly pure, by precipitating the concentrated 75 per cent. alcohol solution with absolute alcohol, and washing well with alcohol and ether, after which it was dried in a vacuum over sulphuric acid. A 75 per cent. alcohol solution

[1] Chittenden: Digestive Proteolysis, p. 62; Hammarsten: Physiological Chemistry, p. 26.

of this was prepared, which, when poured into a considerable quantity of 1 per cent. salt solution, gave the usual precipitate. A clear filtrate, obtained without the use of animal charcoal, exhibited the proteose reactions.

In the course of the work concerning the separation of proteids mentioned above a separation was made of the nitrogen compounds contained in a 1 per cent. salt solution extract of wheat meal, etc., by the method outlined below. Five grams of the material were put into a 250 cc. measuring flask; about 15 cc. of a 1 per cent. solution of common salt were added and the two mixed thoroughly by shaking. The flask was then filled nearly to the neck with the same solution, and in this condition the contents of the flask were shaken at intervals of ten minutes for one hour. At the end of this time the flask was filled to the mark with the fresh salt solution, and the whole thoroughly mixed by shaking. After settling for two hours the liquid was decanted onto a 12.5 cm. dry filter of good quality, leaving the greater part of the solid material in the flask. The liquid was always clouded but, when refiltered through the same filter, generally became perfectly clear. 50 cc. of the clear liquid thus obtained were put into a Kjeldahl digestion flask, 20 cc. of strong sulphuric acid added, and the water removed by boiling, breakage being prevented by protecting the flask by a thin sheet of asbestos cloth. When all water was driven off and the acid ceased foaming, the usual amount of potassium sulphate was added and the nitrogen determination completed. This gives the total nitrogen in the salt extract. 50 other cc. of the clear salt extract were mixed with 250 cc. of strong (94 per cent.) alcohol in a 500 cc. Kjeldahl flask. The resulting precipitate was allowed to settle over night when the liquid readily filtered off. The filter, with such precipitate as it contained, was returned to the flask, and the nitrogen determined, correction being made for a little nitrogen always found in the filter. This precipitate contains the edestin and the leucosin, as was found by suitable reactions. It does not, however, contain the amides, as these are found to be soluble in the amount of alcohol of the strength used in much larger quantities than they ever occur in the amount of wheat taken.

To separate these from the proteids in salt solution, all proteids were precipitated from 50 or 100 cc. of the clear salt extract by adding an excess of a 10 per cent. solution of phosphotungstic acid. By allowing to settle over night, a perfectly clear filtrate was obtained, of which the contained nitrogen was determined in the manner described for total salt extract nitrogen.

If the sum of the edestin, leucosin, and amide nitrogen be subtracted from the total nitrogen of the salt extract, the difference will give the nitrogen which should be credited to the alcohol-soluble proteid which has been dissolved in the 1 per cent. salt solution.

The following table gives the results of such analysis applied to twenty different samples of wheat and mill products.

Table Showing Nitrogen of Compounds Soluble in 1 Per Cent. Sodium Chloride Solution.[1]

Kind of Material.	Total nitrogen in solution.	Edestin and leucosin nitrogen.	Amide nitrogen.	Gliadin nitrogen.
Arkansas Mill Products.				
Patent flour	0.41	0.11	0.03	0.27
Straight flour	0.43	0.13	0.03	0.27
Low grade flour	0.54	0.21	0.05	0.28
"Ship stuff"	0.71	0.31	0.10	0.30
Bran	1.00	0.48	0.23	0.29
Sifted dust (outer bran)	0.50	0.16	0.20	0.14
Porter's Flours.				
Souvenir (extra patent)	0.46	0.11	0.05	0.30
0000 Boss flour (patent)	0.46	0.11	0.05	0.30
Standard flour (straight)	0.50	0.15	0.06	0.29
Strong baker's flour	0.68	0.30	0.09	0.29
Red dog (low grade)	0.97	0.45	0.25	0.27
Winter Wheats.				
Red, Arkansas	0.72	0.31	0.12	0.29
Red, Arkansas (harvest '94)	0.52	0.19	0.10	0.23
Currell, Kansas	0.71	0.30	0.14	0.27
Zimmerman, Kansas	0.68	0.26	0.12	0.30
White wheat, Canada	0.50	0.22	0.07	0.21
Oregon white	0.49	0.20	0.07	0.22
Spring Wheats.				
Red wheat, South Dakota	0.81	0.35	0.17	0.29
Red Fife, North Dakota	0.60	0.25	0.09	0.26
Red Fife, Minnesota	0.64	0.28	0.11	0.25

[1] Figures show nitrogen in each compound in per cent. of 1 gram of substance examined.

An examination of this table will show that the nitrogen from the alcohol-soluble proteid which is entered in the table under the head of gliadin nitrogen, is for 16 of the samples practically a constant. The average for these 16 samples is 0.28 per cent. of nitrogen for 1 gram of material. Many results, which it is thought unnecessary to give, show that the same would have been true if a 10 per cent. salt solution had been used, except that the quantity thus extracted would have been less. There is a great variation in the amounts of the other nitrogen compounds contained in these various samples. The only reasonable explanation of these facts seems to be that an alcohol-soluble proteid which is somewhat soluble in 1 per cent. salt solution and less so in 10 per cent. salt solution exists in considerable quantities in the wheat.

It seems evident that this proteid is gliadin and it appears from the behavior described that gliadin is not changed when it is dissolved in salt solution, but that it remains gliadin. With the exception of being readily soluble in 75 per cent. alcohol, and but slightly soluble in dilute salt solutions, it possesses what have been set aside as the characteristic reactions of proteoses. Apparently it was this body which was found by Osborne and Voorhees in their salt solution extracts and was designated by them as a proteose and a proteose-like body under captions V. and VI.

Four results for alcohol-soluble proteid in the table above vary to a considerable extent from the average of the other sixteen. Of these, one is the sifted contents of the "dust room" of the mill where a portion of the samples were obtained. It consists of the outermost portion of the bran, and contained none of the interior of the grain. The alcohol-soluble nitrogen here obtained is 0.14 per cent. In all these samples the nitrogen soluble in 75 per cent. alcohol had been determined by a method which it is believed gives quite accurate results. In this sample the total amount of nitrogen soluble in hot 75 per cent. alcohol was 0.36 per cent. Of this, 0.20 per cent. should be credited to amides. The difference, or 0.16 per cent., represents that from the total

gliadin in the material, and shows why a greater amount was not in solution in the 1 per cent. salt extract. That this alcohol-soluble proteid of the outermost bran is really gliadin was shown by diluting the suitably concentrated extract with water and with absolute alcohol. In each case a precipitate was produced. Two other samples of the series, which show an unusually low amount of alcohol-soluble proteid in solution were white wheats, each of which was found to contain a very low proportion of gliadin in comparison with the other samples. The remaining irregular sample is an Arkansas red wheat of the harvest of 1894. These include all samples which have been examined in this way.

In the alcohol solution (75 per cent.) gliadin has not been found to exhibit the reactions of proteoses with common salt. The addition of large quantities of salt in bulk, either with or without acetic acid, was not found to cloud it in the least. When salt in solution is added a precipitate will be produced, but in such cases this seems to be attributable, in part at least, to the dilution of the alcohol with water. It has been pointed out by the authors named above, that gliadin is soluble in considerable quantities in pure water but is precipitated from such solutions by the addition of a very small quantity of salt. The experiments here recorded show that the precipitation is not complete.

The solubility of gliadin in salt solutions accounts for the fact that when flour is treated directly with large quantities of such liquid no gluten is formed. It also has an important bearing upon the determination of gluten in wheat or flour by the usual mechanical method of washing away the starch and weighing the residue.

Twelve grams of Porter's "Standard" flour from spring wheat, was made into a dough with 10 cc. of 1 per cent. salt solution, and allowed to stand for one hour. It was then tied in a linen cloth and worked between the fingers in one liter of the same salt solution for one hour. It having been found impossible to obtain a clear filtrate from the solution direct, it was heated nearly to the boiling-point. One hundred and seventy-five cc. of a nearly clear filtrate from this

were evaporated to about 30 cc., and enough strong alcohol added to make the mixture contain 75 per cent. Ten cc. of a perfectly clear filtrate from this showed much cloudiness on adding a few drops of phosphotungstic acid, which cloudiness disappeared on standing, a precipitate being formed. The remainder of the alcohol solution when concentrated gave, in repeated trials, distinct biuret reaction for proteids,[1] the same rose color being exhibited as when gliadin is treated.

It has beed found by a large number of trials, that the so-called true gluten obtained by mechanical washing away of the starch, and computing the remaining proteids from the nitrogen contents of the crude gluten obtained, gives results which are much too low when compared with the sum of the gliadin and glutenin in the sample examined. The explanation is here apparent. An indefinite amount of gliadin is dissolved and washed away. In view of this fact the mechanical method of determining the gluten in wheat and flour is even more unsatisfactory than it has been thought to be.

Having found the above described properties of the alcohol-soluble proteid of wheat, an effort was made to determine whether or not the proteose bodies found by Dr. Osborne[2] in the water or salt solution extracts of oats, rye and barley, and by Drs. Chittenden and Osborne[3] in similar extracts from maize, may be attributable to the alcohol-soluble proteids of those grains. To that end extracts of each were made with 75 per cent. alcohol and with 1 per cent. salt solution.

Of each clear filtered salt solution extract, 25 cc. were mixed with 125 cc. of 94 per cent. alcohol. The resulting precipitates were filtered off, and the clear filtrates were each found to possess the following reactions in common with a solution prepared from wheat in like manner: A precipitate upon dilution either with water or with absolute alcohol; a precipitate or cloud with phosphotungstic acid, which precipitate dissolves on warming and reappears on cooling;

[1] The delicacy of the biuret reaction for this proteid may be increased by using a very small quantity [2 cc.] of the concentrated solution, an equal amount of the strongest caustic potash solution, and, after adding the few drops of copper sulphate, adding also about one cubic centimeter of strong alcohol. After shaking the mixture gently the color will be concentrated in the clear alcohol which rises to the top.

[2] Conn. Exp. Sta. Reports, 1890 and 1894.

[3] This JOURNAL, 13 and 14.

nitric acid does not produce a precipitate in such dilute alcohol solutions.

Of each alcohol extract, 25 cc. were mixed with 125 cc. of 1 per cent. salt solution. A clear filtrate from the resulting mixture gave in each case reactions for proteids. The resulting precipitates dissolved more or less completely on warming, and reappeared on cooling. With nitric acid this solution from wheat gave a slight cloud, which disappeared on warming. With rye solution no change was produced until cooled with ice. A dense cloud then appeared, while a similar tube of liquid without the acid remained perfectly clear. This cloud disappeared on adding strong alcohol as well as on warming. In the solution from barley with nitric acid a similar, but less marked cloud appeared on cooling with ice. No precipitate with nitric acid was obtained in these dilute solutions from either corn or oats. However, certain other reagents gave, in each case, precipitates which dissolved on warming and reappeared on cooling. A nearly clear water solution obtained by mixing a 75 per cent. alcohol extract of corn with a large quantity of water gave a precipitate with nitric acid which did not dissolve, but increased on warming. When, however, a quantity of strong alcohol was added to the liquid, the precipitate immediately dissolved, and remained in solution even when cooled with ice.

With each grain, including wheat, the clear alcohol extract of the meal gave precipitates in the cold with phosphotungstic acid and with tannic acid, each being in solution in 75 per cent. alcohol. In each instance the precipitate dissolved on warming, and reappeared on cooling. With nitric acid the liquid became more or less yellow on boiling, but, as has been shown above, the compound of this acid with these proteids is readily soluble in dilute alcohol. With phosphotungstic acid the cloud, which at first dissolved, reappeared when the liquid was kept near its boiling-point for a short time. In the alcohol extract of corn the precipitate with tannic acid is slight, even with much of the reagent. It may be readily seen if the strong solution of the proteid be diluted with an equal bulk of 75 per cent. alcohol, sufficient reagent added, and the whole cooled with ice. With mercuric chlo-

ride in solution in 75 per cent. alcohol, an abundant precipitate was given in the alcohol extracts of wheat and of oats, which precipitate dissolved on warming, and reappeared on cooling. The alcohol extracts of corn, rye, and barley did not give precipitates with this reagent. It appears, therefore, that these proteids are alike and yet different.

The foregoing facts support the belief that the proteose bodies which have been found in the water or dilute salt extracts of these various grains, except corn, are really the alcohol-soluble proteids, small quantities of which have been carried into solution, and there exhibit their characteristics unchanged. Furthermore, these alcohol-soluble proteids are seen to possess certain properties which have been thought to be characteristic of proteoses.[1]

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SILICIDE OF CHROMIUM.

BY G. DE CHALMOT.

Moissan[2] obtained a silicide of chromium of the formula $SiCr_3$, hy heating silicon with an excess of chromium. When chromium sesquioxide, charcoal and silica (the latter in excess) are heated in an electric arc furnace, a different compound of the formula Si_2Cr, can be obtained. This compound crystallizes in long needles which are gray, and have a strong metallic luster. The crystallizing power of this compound is very pronounced, for the needles were found in a chromium-silicon alloy with only 42.65 per cent. of silicon, and they were very well developed in an alloy with 59.11 per cent. of silicon.

Cold hydrochloric acid and aqua regia have no perceptible effect on this compound, but hydrofluoric acid attacks and dissolves it. This reaction I made use of for determining the composition of the compound. I was unable to obtain a sufficient quantity of pure crystals for analysis. I therefore determined the composition of material to which some silicon

[1] Charles: Physiological Chemistry, 1884, p. 117; Hammarsten, Mandel: Physiological Chemistry, 1893, p. 25; Chittenden: Digestive Proteolysis, 1894, p. 62; Watts' Dictionary of Chemistry, 1894, 4, 331.

[2] Compt. Rend., 121, 624.

adhered, and deducted from the total amount of silicon that part which was insoluble in hydrofluoric acid, and was not chemically combined. I thus found the amount of silicon which was united with chromium. For analysis the material was sifted through linen, and fused with sodium carbonate and potassium nitrate.

	I.	II.
Total silicon	59.11	53.40
Free "	13.84	4.71
Combined silicon	45.27	48.69
Chromium	41.36	45.90

The composition of the crystals therefore is:

	Found.		Calculated for Si_2Cr.
	I.	II.	
Si	52.26	51.48	52.12
Cr	47.74	48.52	47.88

The specific gravity of II. was found to be 4.393.

WILLSON ALUMINUM CO.,
SPRAY, N. C.

Contribution from the Chemical Laboratory of Wesleyan University.

PARAISOBUTYLPHENOXYACETIC ACID.

BY W. P. BRADLEY AND F. KNIFFEN.

Phenoxyacetic acid has been made by Giacosa,[1] by Heintz[2] and by Fritsche.[3] The homologous paraisobutylphenoxyacetic acid was made according to the methods both of Giacosa and of Fritsche. The former method was much simpler in execution, but the latter, as giving much the better yield, is described:

Ten grams paraisobutylphenol were added to 3 grams sodium hydroxide, dissolved in a little cold water; 19 grams chloracetic acid were added to 8 grams sodium hydroxide, similarly dissolved; and the two salts so obtained were brought in pasty condition into an iron pan and heated gently for one hour and a half with constant stirring. The mass became brown, but exhibited none of the deep red color noticed by Fritsche when using the simple phenol. When cool the product was thoroughly neutralized with sulphuric acid, and the watery layer containing sodium sulphate removed. To separate the new compound from the unchanged phenol, ad-

[1] J. prakt. Chem., [2], **19**, 396. [2] Jrsb. Chem., 1859, 361.
[3] J. prakt. Chem., [2], **20**, 269.

vantage was taken of its greater acid strength. The mixture of the two was made distinctly alkaline with sodium carbonate solution and the unchanged phenol was removed with the aid of ether. The resulting straw-colored liquid was evaporated to small bulk, acidified, and extracted with ether. The residue left after evaporating the ether was crystallized twice out of ligroïn, and showed then a constant melting-point of 86°.5. The yield was 9.1 grams, or 66.5 per cent. of the theoretical.

Analysis.

	Calculated for $C_{10}H_{13}OC_2H_3O_2$.	Found. I.	II.	III.
C	69.23	68.92	...	69.08
H	7.69	7.95	7.89	8.03

The new acid is a cream-white solid, practicably insoluble in water. It dissolves very easily in the usual organic solvents, of which many were tried in search of a good purifying medium. Hot ligroïn is the only solvent, however, which deposits clean cut crystals, and this was invariably used. The crystals are radial in structure. They possess a faint, not unpleasant, and characteristic odor, difficult to describe.

Except with mercury and iron, the acid gives salts more or less soluble in water. Those of the alkalies as well as of zinc and magnesium are quite soluble. Solutions of the ammonium salt decompose on boiling with gradual volatilization of the acid, which is betrayed by its odor. The barium and zinc salts were prepared and analyzed.

Barium Salt, $(C_4H_3C_4H_4OCH_4COO)_2Ba, \frac{1}{2}[2\frac{1}{2}]Aq$.—This salt is best obtained by the action of the free acid on barium carbonate suspended in hot water. The resulting solution on evaporation to small bulk, yields the salt ordinarily in the form of small snow-white crystals having a large nucleus surrounded by short, hair-like processes, and resembling somewhat a chestnut burr in appearance. These are permanent over sulphuric acid, but lose half a molecule of water when heated to constant weight at 110°.

Analysis.

	Calculated for $(C_{10}H_{13}OC_2H_3O_2)_2Ba.\frac{1}{2}Aq$.	Found.
H_2O	1.61	1.94
Ba	24.46	24.66

On one occasion a dilute solution of the barium salt deposited crystals having a small nucleus surrounded by relatively large, transparent, radiating arms. These were found, on analysis, to contain two and one-half molecules of water of crystallization. All attempts to secure a further crop of these more highly hydrated crystals failed.

The ordinary variety of the salt dissolves in water at 15° to the extent of 46 parts in 10,000.

Magnesium Salt, $(C_4H_9C_4H_4OCH_2COO)_2Mg,5\frac{1}{2}Aq$.—This salt was prepared by carefully precipitating the barium salt with magnesium sulphate. On evaporation, the filtrate deposited crystals in which fan-like projections radiate from a rather prominent center. The air-dried salt lost its water of crystallization after eight days' drying over sulphuric acid.

Analysis.

	Calculated for $(C_{10}H_{13}OC_2H_2O_2)_2Mg,5\frac{1}{2}Aq$.	Found.
H_2O	18.44	18.47
Mg	4.47	4.40

A magnesium determination was made in the anhydrous salt:

	Calculated.	Found.
Mg	5.48	5.44

The anhydrous salt is hygroscopic. The crystallized salt dissolves in water at 20° to the extent of 13 parts in 10,000.

Esterification of the Acid.—The esterification of the acid proceeds spontaneously to a considerable extent when its alcoholic solutions are allowed to stand even at the ordinary temperature, as may be perceived by the odor when such solutions are allowed to evaporate. The methyl ether, obtained in the usual way by the action of hydrochloric acid gas on the methyl alcoholic solution of the acid, is a wine-colored, viscous liquid of faint, spicy odor. It stiffened in a freezing mixture of ice and salt, but deposited no crystals, even when exposed for some time. Lack of material prevented its purification by distillation, and it was accordingly not analyzed, but was utilized for the preparation of the acid amide.

The Acid Amide, $C_4H_9C_4H_4CH_2CONH_2$.—A portion of the

methyl ether was exposed in a test-tube for five days to the action of twice its volume of concentrated ammonia. The solid cake which had then formed was broken up in a mortar, thoroughly washed with cold water, and crystallized out of very dilute alcohol. The solution becomes milky on cooling, but later deposits the amide in thin, flat, snow-white plates, which when pure, are inodorous and melt at 134°.

Analysis.

	Calculated for $C_{10}H_{13}OC_2H_3ONH_2$.	Found.
N	6.76	6.91

The amide is practically insoluble in cold, difficultly in hot water. In ordinary organic solvents, except ligroïn, it is quite soluble, but separates in poorly defined crystalline masses. From solution in hot ligroïn it separates in massive, well-shaped crystals.

The Anilide, $C_4H_9C_6H_4OCH_2CONHC_6H_5$.—One gram of aniline and two grams of acid were heated for one hour in a short test-tube at 150°. The resulting clear red liquid was poured, while still hot, into cold water. It gradually became viscous, and when stirred with a glass rod became solid. The yellowish-brown mass was washed consecutively with dilute sodium hydroxide, hydrochloric acid, and water, and then dissolved in dilute alcohol. The crystals obtained in this way were somewhat discolored and melted at 97°. They became pure white after a single crystallization out of ligroïn,[1] but the melting-point remained unchanged.

Analysis.

	Calculated for $C_{10}H_{13}OC_2H_3ONHC_6H_5$.	Found.
C	76.33	76.13
H	7.42	7.37
N	4.95	5.13

The anilide is insoluble in water, soluble in organic sol-

[1] It is well known how persistently many anilides retain a slight degree of discoloration. The very striking manner in which the anilide just described was decolorized by the use of ligroïn, suggested the use of the same solvent for other anilides, and it was found in fact that acetanilide can be obtained in snow white needles after a single crystallization from ligroïn, in which, however, it is not very soluble.

vents. Alcoholic solutions yield long individual needles; acetone, clusters of needles; benzene, chloroform, and carbon disulphide, radiating crystalline masses; glacial acetic acid, beautiful fern-like crystals. It appears not to crystallize at all from ether, but is deposited in oily condition.

The Metanitranilide, $C_4H_3C_6H_4OCH_2CONHC_6H_4NO_2$. — This compound was obtained from metanitraniline in the same manner as the preceding. It stiffened, but did not solidify when poured into cold water. It was crystallized twice from alcohol and was obtained in the form of yellowish-brown clusters, which were sufficiently pure for analysis.

Analysis.

	Calculated for $C_{10}H_{12}OC_2H_3ONHC_6H_4NO_2$.	Found.
C	65.85	65.72
H	6.10	6.09
N	8.54	8.72

The compound is so slightly soluble in ligroïn that this solvent cannot be advantageously employed as a purifying medium except for very small quantities. It yields, however, beautiful cream-yellow needles whose melting-point lies between 136°–139°. The compound appears not to melt sharply.

Action of Nitric Acid on the Anilide.—The attempt was made to prepare the ortho and para nitro derivatives of the anilide by direct nitration. The finely divided anilide was introduced gradually into fuming nitric acid cooled in snow, as long as it dissolved freely, and the liquid, after standing fifteen minutes, was thrown upon clean snow. The solid product was washed thoroughly with water, and then dissolved in 95 per cent. alcohol. From this solution several successive crops of crystals were obtained, but contrary to expectation, all of them possessed practically the same melting-point, indicating the formation of a single product only; and this product on analysis was found to contain, not one nitro group, as was expected, but four.

Analysis.

	Calculated for $C_{18}H_{17}N_5O_{16}$.	Found.
N	15.12	15.00

This tetranitro compound is obtained from alcoholic solutions in the form of dull yellow, warty crystals, which melt gradually between 135° and 140°. We were unable to obtain a sharp melting-point. Chloroform, benzene, and acetone deposit the substance as an oil. Most other solvents yield indistinctly crystalline masses. It is not very soluble in ether or alcohol.

Proof was next obtained that the four nitro groups are divided equally between the two benzene rings present in the compound. Four parts of the compound dissolved in alcohol and one part of potassium hydroxide, also dissolved in alcohol, were brought together and boiled three-quarters of an hour. After evaporating the greater part of the alcohol, water was added. The nitraniline thus precipitated was removed by aid of ether, and was crystallized, after evaporation of the latter, twice from alcohol. Small, bright, lemon-yellow crystals were obtained, melting sharply at 176°.5, which give the red coloration when boiled with dilute potassium hydroxide, which is characteristic for *o-p*-dinitraniline.

It should have been an equally easy task to locate the other two nitro groups in the benzene ring belonging to the paraisobutylphenoxyacetic acid, but this result was prevented by unexpected difficulties in the purification of the dinitro acid. The compound exhibited a stubborn tendency to separate from its solutions as a gummy mass, containing, to be sure, in most cases, small crystals, but these crystals in turn show the same tendency on recrystallization, so that no direct proof of their composition could be obtained. There seems no doubt, however, as already indicated, that the product obtained by the direct action of cold nitric acid on the anilide is paraisobutyldinitrophenoxyacet-*o-p*-dinitranilide,

$$C_4H_4(NO_2)_2C_6H_3O.CH_2CONHC_6H_3\begin{matrix}NO_2\ (2)\\NO_2\ (4)\end{matrix}.$$

The Toluides, $C_4H_9C_6H_4OCH_2CONHC_6H_4CH_3$.—The ortho and para toluides of the acid were also prepared. The melt containing the ortho derivative gave, when poured into water, a blue-black, solid mass, which crystallized out of ligroïn in long, flat, white blades, which melt at 91°. It dissolves

readily in organic solvents, and is deposited from most of them, even after complete evaporation of the solvent, in well-formed crystals, usually of dendritic structure. Dilute alcoholic solutions yield only oil drops.

The paratoluide is dull gray before purification, and snow-white after. The crystals obtained by the use of ligroïn as a solvent resemble strongly those of the ortho compound, but melt at 122°. From other solvents indistinct crystalline masses are usually obtained, except from alcohol, which yields, as with the ortho compounds, oil drops.

Analysis.

	Calculated for $C_{18}H_{13}OC_6H_9ONHC_6H_4CH_3$.	Found. Ortho.	Para.
C	76.77	76.54	76.59
H	7.74	7.63	7.36
N	4.71	5.05	5.07

Paraisobutylphenoxyacetphenylhydrazide, $C_4H_9C_6H_4OCH_2CONHNHC_6H_5$, was obtained by heating the methyl ether of the acid with its own weight of phenylhydrazine four hours at 110°. The reaction proceeds rapidly at first with ebullition. The resulting product solidified on cooling to a mass resembling candied honey. When crystallized from alcohol or glacial acetic acid, it yielded colorless crystals melting sharply at 171°.5.

Analysis.

	Calculated for $C_{18}H_{13}OC_6H_9ON_2HC_6H_5$.	Found.
N	9.40	9.59

The hydrazide is easily soluble in the ordinary solvents, except ligroïn, in which it dissolves but sparingly.

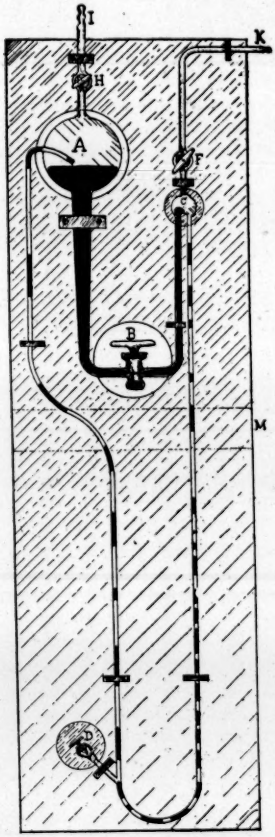
Contribution from the Sheffield Laboratory of Yale University.

XLVII.—ON A SIMPLE AUTOMATIC SPRENGEL PUMP.

By B. B. Boltwood.

The following description of a simple modification of the Sprengel pump, the advantages of which are compactness,

convenience, and speed in obtaining vacua of high exhaustion, may be of interest to both chemists and physicists.



The apparatus, which is fastened to a board 60 cm. in length and 18 cm. in width, consists of the bulb *A*, 6 cm. in diameter, connected by means of the tube *ABC*, in which is situated the stop-cock *B* with mercury seal, with the small bulb *C*, about 2 cm. in diameter, into which the tube *KC*, connected with the vessel to be exhausted, opens, and from which extends the fall-tube *CD*, 50 cm. in length. The continuation of *CD* is the return tube *DA*, which extends into the interior of *A* for about 3 cm. The bulb *A* is about one-third full of *clean*, *dry* mercury.

The operation of pumping is as follows: The tube *I* is connected by means of suitable thick-walled rubber tubing with a water-jet pump, which will give a vacuum of about 40 mm. or less, and the cocks *H* and *F* are opened, the cock *B* being closed. The vessel connected at *K* is then partially exhausted, and, when the pressure has reached about 40 mm, the stop-cock *B* is opened, and the mercury is allowed to flow slowly from *A*

to *C*. It falls into the fall-tube *CD*, as in an ordinary Sprengel pump, carrying with it the air from *C*. The vent-cock *D* is now opened carefully, and a quantity of air permitted to enter, sufficient to sweep the mercury rapidly up the return-tube *DA* into *A*. The end of this tube is curved downward, slightly, to diminish the spattering of the mercury. The vent-cock *D* requires no special mention. Any appliance for regulating the air-supply suffices, a thick-walled rubber tube, with pinch-cock, having been used with perfectly satisfactory results.

The operation of the pump is now perfectly continuous.[1] The mercury falls constantly from *C* into the fall-tube, and is as rapidly returned to *A*. A careful adjustment of *B* and *D* as the exhaustion advances gives a maximum efficiency.

The fall- and return-tubes should be 2.5 mm. inside diameter, as advised by Sprengel.[2]

With a pump of this description, after working for ten minutes, vacua so low that they could not be read on an ordinary manometer, were obtained, and electrical phenomena in tubes which had been exhausted gave evidence of extremely low pressures.

With suitable drying attachments, at *K*, *I*, and *D*, tubes for cathode ray experiments could undoubtedly be prepared.

The board supporting the pump may have a bracket on the back in the position shown by the dotted lines at *M*, which permits of its being firmly secured by means of a wood screw, to the edge of any bench or lecture table, while the small size and weight of the whole apparatus permits of its being freely moved from place to place.

The quantity of mercury required by the pump is very small, and, since it comes in contact with no rubber or grease, and is protected from dust, its contamination is entirely prevented.

The stop-cocks *B* and *F* are closed before the vessel connected with *K* is removed.

[1] The cut shows the pump in operation.

[2] J. Chem. Soc., 1865, 15.

REVIEWS.

THE PRACTICAL METHODS OF ORGANIC CHEMISTRY. By LUDWIG GATTERMANN, PH.D. Translated by William B. Shober, Ph.D., Instructor in Organic Chemistry in the Lehigh University. New York: The Macmillan Company.

This book, which is a translation of Prof. Gattermann's valuable work is, in the words of the translator, "intended for those students of chemistry who have not yet become sufficiently familiar with scientific German to be able to read it accurately without constant reference to a dictionary." The first part of the book contains clear and detailed descriptions of the various operations necessary in connection with the preparation of organic compounds, and also the best methods for their analysis. The part devoted to organic preparations is somewhat similar to the works of Fischer and Levy on this subject; but it is more general in its nature. The translator has followed the methods of classification adopted by Prof. Gattermann and has reproduced the cuts of apparatus in the German edition. He has had the benefit of Prof. Gattermann's suggestions as to the correction of some inaccuracies in the German edition and has introduced a table to facilitate the calculation of nitrogen in organic analyses. The translation is excellent, and the book can be recommended as a valuable addition to the English works on organic preparations.

J. E. G.

NOTES ON QUALITATIVE ANALYSIS, arranged for the use of students of the Rensselaer Polytechnic Institute. By W. P. MASON, Professor of Chemistry. Third Edition. Easton, Pa.: Chemical Publishing Company. 1896. Price, 80 cents.

This manual differs from others written for the same purpose, in its brevity. So few reactions are given for each metal that the book seems available only for the most elementary instruction. The author even omits all methods for analysis of the phosphates of the alkaline earths as too difficult for beginners.

The other feature of this book is found in frequent references to chemical works and journals. It would seem that if a student is not ripe for a method of detecting aluminium in the presence of phosphates he would derive little benefit from dipping into chemical literature, but the author's experience has evidently led him to a different conclusion.

E. R.

CHEMISTRY FOR BEGINNERS. By EDWARD HART, Professor of Chemistry in Lafayette College. Third Edition, revised and greatly enlarged. Easton: Chemical Publishing Company. 1896. Price, $1.50.

The very worthy object which Dr. Hart had in mind in preparing this book was to provide the beginner with directions for a large number of experiments requiring but simple apparatus, and at the same time with a sufficiently detailed statement of elementary chemical phenomena to serve for a "beginner's course."

The experiments, which number about 220, are in the main well chosen. The chief adverse criticism to be passed upon them is that the author in his desire to be concise has, at least in many cases, given too little space to the discussion of the method of procedure and of the point to be illustrated. It is poor economy to cut down this portion of a book intended for beginners, since it at once throws a greater burden upon the instructor, and generally results in ignorance on the part of the student as to the object for which the work is done, even when the experiment in question is, ordinarily speaking, successful.

The descriptive portion of the book has apparently been carefully brought up to date. Modern commercial methods for the preparation of chemical substances are, as a rule, clearly and concisely described. The commercial application of many chemical products is treated in an especially satisfactory way. But far too many compounds are mentioned—they can hardly be said to be described—for a student to be able to consider with profit at the beginning of his course. This is especially true of that portion of the book devoted to carbon compounds: a distinct lack of proportion may be said to characterize the work from this point of view.

Of the method of handling the theoretical side of the subject, much less can be said in commendation. The beginner is confronted at the outset with theoretical points for which he has had no suitable preparation. As a single instance, he is told in Chapter III. that the difference between oxygen and ozone is supposed to lie in the fact that their molecules contain two and three atoms, respectively, and that their symbols are O_2 and O_3; whereas no explanation of atoms, molecules, symbols, etc. is given for several chapters. Again, many equations are given as explanatory of certain general phenomena, which do not represent actual reactions. Thus, as showing the production of hydrogen by substitution is cited the action of silver, lead, copper, bismuth, and chromium—among other metals—upon nitric acid.

Finally, statements constantly appear which should not have been made without qualification; in these cases also the author's conciseness results in inaccuracy. For example, we are told that "the modern theory of chemistry is due to Lavoisier;" that "life is a process of oxidation in which food is the fuel and carbon dioxide is thrown off to mix with the air;" that "when carbonic acid is acted upon by a metal which replaces one atom of hydrogen, such as sodium, we get first a carbonate containing one hydrogen atom, thus $NaHCO_3$. If two atoms of sodium act upon carbonic acid both hydrogen atoms are replaced and we have Na_2CO_3."

W. W. R.

MANUAL OF DETERMINATIVE MINERALOGY, with an introduction on Blowpipe Analysis. By GEORGE J. BRUSH, Director of the Sheffield Scientific School of Yale University. Revised by SAMUEL L. PENFIELD, Professor of Mineralogy in the Sheffield Scientific School of Yale University. New York: John Wiley & Sons. 1896. Price, $3.50.

Prof. Brush's book is so favorably known that it needs no praise; suffice it to say that Prof. Penfield has thoroughly revised the first half of the book, introducing new methods, and prescribing the methods incidental to the tests for the elements in detail. A revision of the tables for the determination of minerals is promised for a future edition. In the present edition half of the book is made up of these tables taken from a former edition by Prof. Brush. It is to be regretted that the publisher did not print the tables in good type; they are printed from worn out plates, and partially illegible words or letters can be noted on every page.

E. R.

CHEMISTRY IN DAILY LIFE. Popular Lectures by DR. LASSAR-COHN, Professor in the University of Königsberg. Translated by M. M. PATTISON MUIR, M.A. London and Philadelphia: J. B. Lippincott Co. Price, $1.75.

These lectures treat of many subjects. The air, combustion, flame, illuminants, plant life and agriculture, foods, explosives, tanning, dyes, potash, soda, soaps, glass, ceramics, photography, the metals and alkaloids are the principal ones. Professor Lassar-Cohn has succeeded in writing a book which is simple and clear enough to be understood by any person of intelligence, and yet the book is scientific in spirit and up to date in detail. It should be of particular value and interest to college students who have heard a course of lectures on chemistry, partly as a review, partly as emphasizing the practical applications of reactions and principles with which they are familiar.

E. R.

HANDBOOK FOR THE BIO-CHEMICAL LABORATORY, including Methods of Preparation and Numerous Tests Arranged Alphabetically. By JOHN A. MANDEL, Professor of Chemistry at the New York College of Veterinary Surgeons, and Assistant to the Chair of Chemistry, etc., at the Bellevue Hospital Medical College and the College of the City of New York. First Edition. 101 pp. New York: John Wiley & Sons. London: Chapman & Hall.

This small handbook, designed principally for students, is divided into two parts. Part first, consisting of 61 pages, gives concise and accurate methods (in some cases more than one) for preparing the most important substances found in the tissues and fluids of the animal body; in some instances methods for the synthetic preparation of these substances are also given. The author does not claim originality in any of these methods, and states in his introduction that the methods have been taken from the most recent, important works on physiological chemistry. Either the empirical or structural formula is given with the name of the substance isolated. It seems to the writer of this notice that in a book of this kind, designed for students, it would have been well to introduce chemical equations wherever practicable, or to introduce interrogation marks after certain directions, thus bringing these points to the attention of the student. Otherwise the manipulations are mechanical and the directions are equivalent to so many receipts in a cook-book.

Part second, consisting of 40 pages, is taken up with some 200 well-known tests used in bio-chemical and physiological chemical work. These are arranged in alphabetical order, and the name of the person who suggested the test, or the name under which it is ordinarily known is given in each case. Such a list has long been desired by workers in this field; and it is an important addition to bio-chemical laboratory literature.

The value of the book lies in its compactness. It gives students in a few pages all the data really necessary for immediate work, and thus saves time which would be used in searching for methods and tests in larger works. T. B. A.